PROCEEDINGS OF HAZMACON 86

HAZARDOUS MATERIALS MANAGEMENT CONFERENCE AND EXHIBITION

April 29 – May 1, 1986
Anaheim, California

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ASSOCIATION OF BAY AREA GOVERNMENTS

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Hazardous Materials Management Conference and Exhibition

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REGULATION AND LOCAL PLANNING

HAZARDOUS MATERIAL PREPAREDNESS
FOR THE RURAL COUNTY

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One result of the use of hazardous materials is the need to design and implement a preparedness program for dealing with emergency response to spills and releases. In many counties the political desire to see this issue addressed effectively conflicts with an increasingly tight fiscal situation. Despite current political interest, programs must be cost-effective in order to constitute good public policy which can be maintained indefinitely.

A common perception is that the emergency response solution is to first form a centralized, technically trained "HazMat" team. This approach is strengthened by the availability of state financed hazardous material equipment. An analysis of the situation in a rural setting leads to rejecting such a program, particularly when it is based only on "common" wisdom, or worst-case scenarios.

This paper will outline the analysis that led San Joaquin County to adopt an approach that emphasizes the first responder, both public and private. After looking at incident characteristics in the County it was felt that this would provide effective response and a firm base for adding further capabilities if needed.

THE RURAL CHEMICAL INCIDENT: PROBLEMS AND CHARACTERISTICS

Rural chemical accidents tend to repeatedly present the same response requirements. Experience has shown that these requirements can be met effectively by the trained first responder. The key to public safety is general awareness, and knowledge of procedures, by all responders. In addition, the isolated nature of many rural accidents means that the first responder is often the primary person at risk.

Response Problems

The problem that most often determined the length and disruption of an incident was getting known toxic chemicals cleaned up. Since a

"HazMat" team typically does not perform this function, its availability does not eliminate the need to call a private contractor. However, some basic training of first responders and dispatchers can make a difference by ensuring more rapid assessment, notification, and access to appropriate funding sources.

The second most troublesome problem encountered was identification of unknown chemicals. However, the relatively isolated nature of most rural incidents meant that a delay in obtaining identification did not entail a significant disruption of traffic or people's activities. Therefore, the less expensive option of providing health officials with a simple HazCat Kit and basic protective equipment allowed the great majority of these substances, mainly powders, to be identified and dealt with promptly. The disruption from the occasional incident where a private company had to be called was minimal.

Technical containment, or rescue, in a toxic environment was a very rare occurrence. Rural county history has shown that expenditures to maintain this capability would not be cost-effective. The area where this could most likely be required is at fixed facilities. Better oversite of chemical handlers to ensure that they have appropriate capabilities on hand would be a better initial approach to this need.

Public Safety Requirements

Ensuring public safety also pointed to the first responders as a better solution than a centralized team. In past incidents, public safety was ensured by rapid assessment, isolation of the spill area, and evacuation of potentially affected areas. Prompt assessment and action by the first responder, even if trained at a lower level, is more valuable than assessment by a more highly trained responder arriving later. This has even been seen in some of the worse accidents in the state. Technical training and equipment are just not as relevant to these actvities as the preparedness of the general response organization.

Other safety problems seen occasionally were the injury or contamination of first responders, the need to treat contaminated victims, and accidents caused by chemical handlers who lacked training or equipment. The first two areas pointed again to the need for better first responder training in law, fire, and medical organizations. The handler accidents are an area where more government attention could greatly improve overall county preparedness.

THE "HAZMAT" TEAM IN THE RURAL SITUATION

As pointed out, a technically trained team is not required for the vast majority of incidents in rural areas. However, creating a team for that rare need would be appropriate if the costs were low and significant drawbacks were not present. That is not the case when examined closely.

First, the expense of maintaining a team for a rural county will be substantial, even if the equipment is provided by the state. Ensuring proper liability in today's insurance environment will constitute a significant cost. In addition, the rural county's highly fragmented jurisdictional structure is under financial stress already. The difficulty of finding a jurisdiction which could spare individuals to staff a county-wide team means that additional personnel, and therefore costs, would probably have to be added. Finally, equipment replacement and training costs would also be on-going.

Beyond the point that a team is costly, there is the problem of maintaining proficiency. It will be difficult for team members to maintain the degree of proficiency that must be expected in this field given the response requirements and frequency seen in the past. This creates a higher liability risk as well as the potential for an ineffective response if a complex incident does occur.

Finally, by first forming a technically trained team, there is the danger that less expensive, or more effective, alternatives for dealing with common response problems will be neglected or overlooked. In particular, money, time, and attention will be drawn to the team due to its high visibility. Less visible issues, such as first responder training, or follow-on programs, such as business oversite, could suffer accordingly.

PREPAREDNESS FOR THE RURAL COUNTY

San Joaquin County's program aims to provide efficient response that is cost-effective. By not becoming unnecessarily involved in adding expensive response capabilities, it has been possible to commit more resources to new legal requirements. In particular, the county is now able to commit time and money to thorough implementation of AB2185, which will improve county mitigation efforts and response significantly.

Training

The basis of our approach is better training for all first responders. For public agencies, this consists of county specific courses that stress responder safety, assessment, notification, and public safety. While there are numerous training courses in the state, these are generic, and therefore not completely sufficient or accessible for the first responder. Training must include county specific procedures and responsibilities. In addition, while other training courses stress the technical aspects of hazardous material response, these courses also cover areas which tend to be taken for granted, like evacuation techniques.

The second area for improving preparedness is the private first responder. Instead of spending funds on an expensive team, resources will be used to effectively oversee chemical handlers to ensure that they have the equipment and training necessary to mitigate their

spills. This will be far more effective in the long run and will help place the costs for preparedness at the source of the problem.

Finally, agencies such as Local Health and the Agricultural Commissioner are utilized to provide additional expertise. Inexpensive training, and some simple equipment, handles the majority of identification, and assessment needs in the county. Over the past three years, the cost of using contract companies for the rest of the incidents has been far below the cost of maintaining a specialized team.

Disaster Preparedness

While the risk of a major chemical accident is less likely for the rural county, it is a possibility that must be considered. Unfortunately, the formation of a "HazMat" team is often seen as the panacea to chemical accident response, with the result that critical areas of preparedness are neglected. The key to preparedness for this eventuality lies in the difficult task of maintaining a coordinated and effective county emergency organization. A functional emergency operations center, regular drills, and close cooperation among jurisdictions is far more important than just the presence of technically trained individuals. The County's approach, by stressing this overall response "organization", has the spill-over benefit of increasing preparedness for other disaster response needs.

CONCLUSION

It would be nice if local government could cover all the potential problems associated with hazardous material response with optimum solutions. Today's tight fiscal situation means, though, that cost-effectiveness must enter the picture. Careful analysis prior to commitment of public funds will avoid costly mistakes, and ensure the most efficient possible response. For the rural county, such an analysis rejects the solution of forming a "HazMat" team, for practical as well as cost reasons. It is felt that the alternate program adopted will lead to efficient response without costly overkill.

PROTECTING UNDERGROUND WATER SUPPLIES IN SANTA CLARA COUNTY

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HISTORICAL GROWTH OF WATER DEMAND

Back at the turn of the century, the Santa Clara Valley floor was covered with acres of prosperous farmland. Frustrated gold seekers had come to farm the area because of the relatively flat terrain, the rich soil, and the favorable climate combined with a readily accessable, abundant groundwater supply. The valley floor was soon perforated with thousands of agricultural and domestic wells.

The steadily growing demand for water eventually led to the necessity of augmenting the natural groundwater yield of the basin. By 1935, a series of six new dams were completed, enabling winter rains to be captured and, through a system of canals and recharge facilities, percolated into underground aquifers. This marked the beginning of a systematic management of the groundwater basin.

Between 1940 and 1950, Santa Clara Valley's population nearly doubled, reaching almost 300,000 in 1950. Ironically, for the same reasons that agriculture prospered in the valley, industrial growth gradually crowded farmers out of the valley, confining orchards and row crops to smaller and smaller portions of the valley. The demand for water again out stripped the supply.

In 1947, bond issues were passed to build two more dams in the county. In addition, state legislation created a new countywide water district in 1951 empowered, among other things, with the ability to contract for the purchase of "imported" water. In 1965, the first deliveries from the State Water Project were made through the South Bay Aqueduct. Finally, in 1977, a contract for the purchase of water from the Bureau of Reclamation was signed with the first deliveries scheduled for 1981.

Industry continues to prosper in the area and the population continues to grow. Today, the Santa Clara Valley Water District (Water

District) is responsible for insuring an adequate water supply to the 1.4 million residents of Santa Clara County. The underlying groundwater basin remains an integral part of that water supply.

WATER SUPPLY

Currently, the total water demand in Santa Clara County is nearly 400,000 acre-feet per year. It is satisfied by three sources of supply; 1) water imported from San Francisco Water Department's Hetch Hetchy Water Project, 2) water imported from the State Water Project, and 3) locally developed surface and groundwater. In addition, water will soon be available from the San Felipe Division of the Federal Bureau of Reclamation water project facilities.

About 80,000 acre-feet per year of water is delivered to areas along the northern boundary of the county from Hetch Hetchy Aqueduct. This water is purchased by water retailers directly from San Francisco Water Department and requires no treatment.

The State Water Project supplies about 100,000 acre-feet of water per year to Santa Clara County. Most of this is treated at the Water District's two treatment plants and subsequently sold to some of the nineteen water retailers in the county. About 20,000 acre-feet is used for either groundwater recharge or direct surface diversions.

As mentioned above, local water conserved in the eight Water District operated reservoirs in the county is used to augment the natural groundwater basin yield through artificial recharge facilities - ponds constructed in gravelly formations for purposes of percolating water into the underground aquifer materials. Total groundwater pumpage in the county is about 220,000 acre-feet per year - about 60 percent of the total county water supply. Most of that water is introduced by artificial recharge - the basin being used as an economical means of treatment, storage and distribution to areas of demand.

HYDROGEOLOGY

There are three groundwater subbasins in Santa Clara County - the Santa Clara, the Coyote, and the Llagas - as shown in Figure 1. A groundwater divide is located between the Coyote and the Llagas subbasins - that is, water flows to the north and to the south from that point. The Llagas subbasin is, therefore, essentially isolated from the two northern subbasins.

Groundwaters in the Coyote subbasin flow northward into the Santa Clara subbasin. The Coyote is a shallow subbasin characterized by very course grained materials. Groundwater movement is rapid in this area and it is, therefore, an excellent recharge area.

The Santa Clara subbasin is by far, the largest of the three subbasins. Groundwater in the Santa Clara generally flows radially from the surrounding foothills towards the bay. A predominant feature of

this alluvial (stream deposited) and lacustrine (lake deposited) geologic materials comprising this subbasin is an extensive clay layer located about 100 feet below the surface and extending radially from the bay to the boundary shown on Figure 1.

In the generalized cross section shown in Figure 2, it can be seen that the clay layer divides the basin into three zones - the confined aquifer, the overlying unconfined aquifer, and the forebay zone. The confined aquifer is the one from which most of the water production is withdrawn. It is relatively protected from surface contamination by the overlying clay layer. The unconfined aquifer is tapped by a number of private wells that are used mostly for outside irrigation purposes. The forebay zone, located around the perimeter of the valley floor, is a critical region of the ground basin. Water from this zone, and the overlying land area, is the sole source of replenishment of the deep, confined aquifer zone.

CONTAMINATION

Contamination of soil and groundwater from leaking underground storage tanks presents a serious threat to the groundwater basin underlying Santa Clara County. As discussed above, the groundwater basin is a key element of the water supply in the Valley. Almost all of the underground tanks can be divided into two main categories, depending on the type of material stored - organic solvent tanks and fuel tanks.

Organic Solvent Leaks

About 20 years ago, the silicon chip industry was just getting started in Santa Clara Valley. Highly touted as "the clean industry", as opposed to smoke stack types of industry, the electronics firms were welcomed to the Valley and today the industry has grown to the point where the northern part of the Valley is now commonly referred to as Silicon Valley. It wasn't until quite recently that we realized we were literally overlooking a serious environmental hazard associated with the industry.

In 1981, a large electronics firm located in the southern end of the Valley reported to the Regional Water Quality Control Board (Regional Board) the loss of about 60,000 gallons of waste solvents and water from an underground storage tank farm. A week later, on December 7, 1981, Great Oaks Water Company well number 13 was shut down after detecting contamination with trichloroethane (TCA) at a concentration of 5,800 ppb.

During the next year, the Regional Board conducted extensive surveys of all businesses that might have underground solvent storage tanks. Solvents were considered a high priority because of their high solubility in water, their specific gravity, and their persistence as compared to petroleum products. They found that a significant number of them had leaking tanks. Today, the Regional Board is overseeing the investigation of about 90 sites with soil and/or groundwater contamination originating mostly from organic solvent tanks.

Fortunately, most of the cases are located in the Silicon Valley area, which overlies the region of the deeper aquifer that is somewhat protected from surface sources of contamination by the clay layer mentioned earlier. The main problem in this area is from the potential interaquifer connection through the thousands of abandoned agricultural wells.

Although most of the cases are located in Silicon Valley, there are two important cases located in the forebay zone of the basin where Coyote Subbasin joins the Santa Clara Subbasin. These cases are quite significant not only due to their magnitude and the high permeability of the soils in that area but also because that area recharges the deeper confined aquifer. Due to the critical nature of their location, they have received a high priority response and the plumes of contamination are now under hydraulic control by means of strategically located extraction wells.

Fuel Leaks

Contamination from petroleum products is considered somewhat a lower priority than that from organic because of several factors. First, because of relatively low specific gravity, petroleum products tend to float on the water and are, therefore, easier to remove from the groundwater system. Also, they are considerably less persistent and less toxic than organic solvents so their presence is not considered as great of a hazard to the groundwater quality. Lastly, at the time of the Regional Board survey, petroleum products were generally considered insoluble in water. However, since then research of underground tanks has shown that certain toxic components of the fuel products are, in fact, soluble in water and, therefore, leaks that occurred several years ago can pose a serious groundwater quality problem. It was decided at the time, though, because of staffing shortages at the Regional Board, to allow the cities to determine the integrity of the fuel tanks in the Valley through the implementation of the respective Hazardous Materials Storage Ordinance (HMSO) which were, by then, soon to be adopted. The local HMSO's require testing and monitoring of underground tanks similar to the mandate of the later developed state Sher Bill.

The implementation of the HMSO is roughly 50 percent complete on a countywide average, and about 400 leaking fuel tanks have been discovered. Contamination from these incidents range in magnitude from slight soil contamination directly beneath the tank to massive soil and groundwater contamination which will require months of investigation and remedial action to define and cleanup. Initial regulatory response, such as overseeing soil sampling and removal operations, has been provided by the city of jurisdiction so far. However, the cities are not staffed for the purpose of overseeing the definition and cleanup of the many cases of extensive soil and groundwater contamination. Even their current level of involvment goes beyond their original intentions and virtually all cases are referred to the Regional Board for followup review. However, the Regional Board's limited staff has allowed only limited response and, since additional funding is apparently not

forthcoming from the state, the Water District is, at the time of this writing, analyzing the necessary funding and authority mechanisms to allow the investigation to proceed under Water District staff oversight.

GROUNDWATER QUALITY MONITORING AND PROTECTION PROGRAMS

In addition to direct monitoring of underground storage tanks, subsequently mandated by the state Sher Bill and the groundwater quality monitoring required by Assembly Bill 1803, several supplementary monitoring and protection measures have been taken in Santa Clara Valley to help insure that the generally pristine quality of the groundwater basin is maintained.

Private Wells Sampling

While state Assembly Bill 1803 requires that all public water systems test representative wells for the presence of organic contaminants, there is no guarantee for the many private well owners that the well water on which they depend is safe for consumption. As mentioned earlier, small private wells generally are shallow and draw water from the unconfined aquifer, or if deeper, draw water from both the upper and the lower aquifer. In contrast, high yielding municipal wells are constructed to prevent shallow groundwaters from entering and draw only from the deeper, more protected water bearing materials. Private wells are, therefore, much more susceptible to contamination from surface sources. In fact, in recent months, several private wells in the Silicon Valley area have been taken out of service as a direct result of organic solvent contamination originating from underground tank leaks in the area. Those incidents served to heighten the concerns and anxieties of an already uneasy public.

Partly in response to public's demands for information, and in part, due to the Regional Board's desire for monitoring data to augment that collected by leaking underground tank owners, the Santa Clara County Health Department, in cooperation with the Regional Board and the Water District, recently sampled 171 wells in the vicinity of known leaks. The funding for that program was from Regional Board assessments on owners of facilities with on going groundwater investigations. The sampling effort revealed that thirteen of the private wells had some level of organic chemical contamination - five with concentrations of chemicals over state action levels.

Concurrently, a task force of local political and regulatory agency leaders were pursuing state funds for an expanded private well testing program in the Valley. Those funds have been appropriated and further testing is in progress in critical, high risk areas of the basin.

Abandoned Well Sealing

The confining clay layer underlying the Silicon Valley area, as mentioned earlier, offers a natural protection to the deeper, heavily pumped aquifers. However, there are estimated to be thousands of abandoned agricultural wells in the area left over from the previous era of farming in Santa Clara Valley. As new development occurred, these wells were, as a general rule, simply cut off just below the surface to make room for office buildings, houses, and other improvements on the land. This practice has left us with a clay layer perforated with rusting, often times multi-perforated, well casing to serve as conduits between the shallow and deeper aquifers. Since the water table in the shallow aquifer is generally higher than the hydraulic head in the deeper aquifer, the tendency is for water to travel down through these conduits. Therefore, any wells in the vicinity of contamination plumes in the upper aquifer can be a real threat to the quality of the deeper aquifer.

In order to minimize that threat, the Water District embarked on an ambitious program several months ago intending to locate and seal abandoned wells in the vicinity of known plumes of contamination. That program is still in progress and, at the time of this writing, about 100 high risk wells have been sealed.

As this program developed, the Water District sought state legislation to modify the District Act to require the sealing of abandoned wells by the well owner when those wells are determined to constitute a water contamination hazard. That effort was successful in the passage of Assembly Bill 689. Therefore, after the ongoing well sealing effort expires, Water District funds will not have to be expended for sealing private abandoned wells and the burden of the responsibility will rest on the well owner.

PUBLIC PARTICIPATION AND EDUCATION

As all of the programs to cleanup and prevent groundwater contamination in the Valley have developed in the last few years, public participation has been, and continues to be, a key factor in their success. Many of the questions that arise, especially with regard to the cleanup of contamination from leaks, cannot simply be answered by technical analyses alone. The decisions that must be made involve broad public policy issues and, as such, require the input of an informed public. Public participation must be included and, in fact, should be encouraged at major decision points in cleanup activities as well as in related legislative and regulatory efforts concerning public health issues. The public has a right to be involved in decisions affecting their health.

In order to have the input of an informed public it is, therefore, a primary responsibility of all involved agencies to collect and objectively disseminate important information as it becomes available. The dissemination of this information requires a major public education

effort. Admittedly, this effort imposes more demands on the staff time of, very often, already under staffed agencies. However, the lack of such an effort can potentially lead to a public perception that attempts are being made to somehow conceal or "cover up" important facts regarding sensitive issues. Such a public perception might ultimately undermine the effectiveness of such agencies.

In Santa Clara County, public education has been an integral part of all of the activities of the various agencies involved in groundwater protection programs. The Regional Board has been especially effective in this area by holding public hearings on each of the toxic cases as important decisions are made regarding the remedial action plans. At the public hearings, a public testimony is taken on each case after Regional Board staff explains the facts of the case.

Examples of other education efforts have been more general in nature. The Environmental Protection Agency for example, published a White Paper several months ago as part of a study of the relative risk to human health posed by groundwater contamination. The White Paper attempted to summarize all of the drinking water quality issues and related corrective efforts in the Valley. The California Department of Health Services, in 1984, conducted an extensive study of the possible health effects on a community at the south end of the Santa Clara subbasin of consuming water tainted with trichlorethane. Preliminary results of that study have been released and further work is still being done in that area. Finally, the County Health Department, the Regional Board, and the Water District recently cooperated in the private well sampling program mentioned previously, intended, in part, to inform the well owners of the quality of their water.

In conclusion, continued open lines of communication between the public and the various agencies having jurisdiction in Santa Clara County help to reassure the public that every effort is being made to minimize their exposure to hazardous contamination in drinking water.

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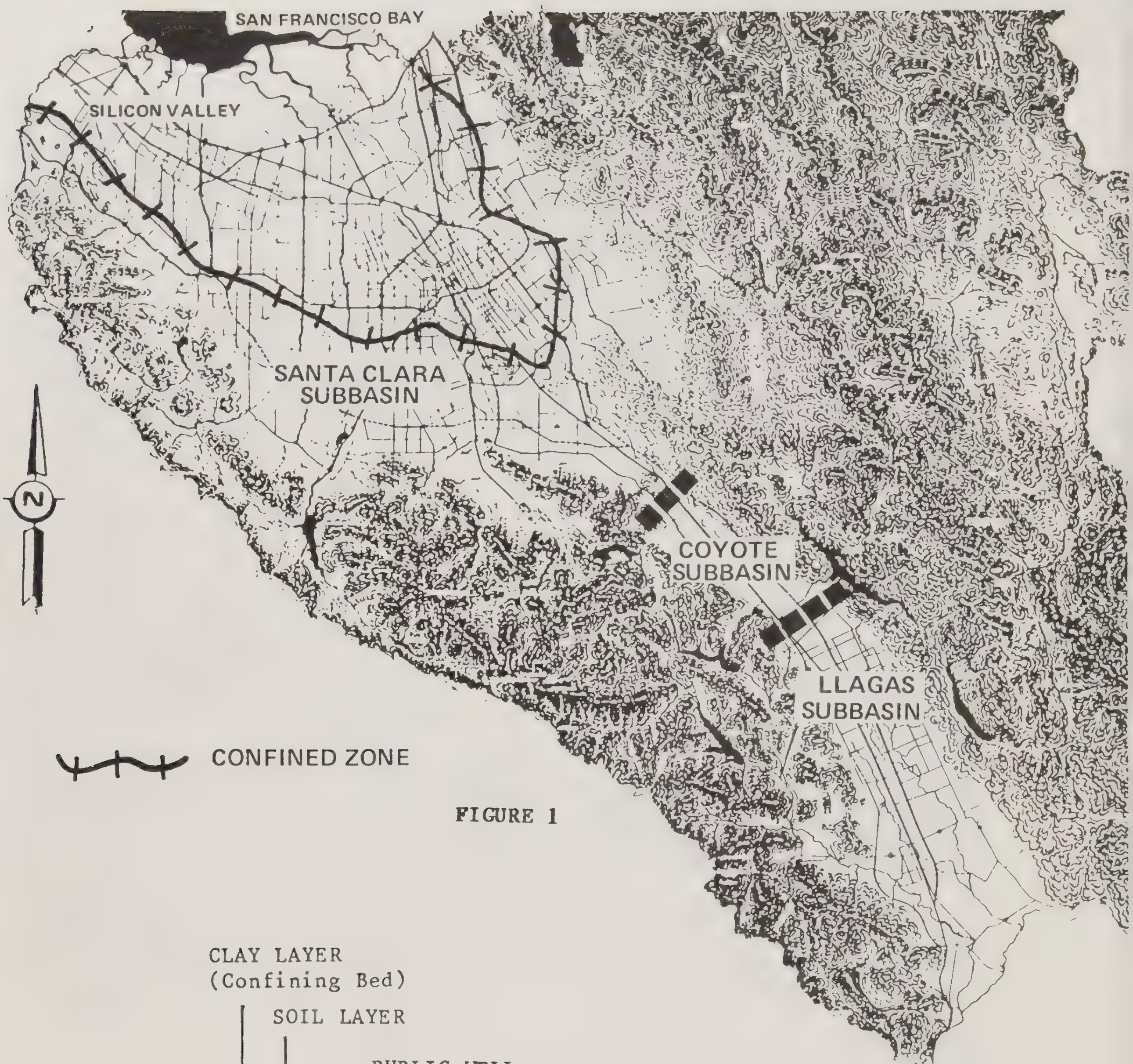

FIGURE 1

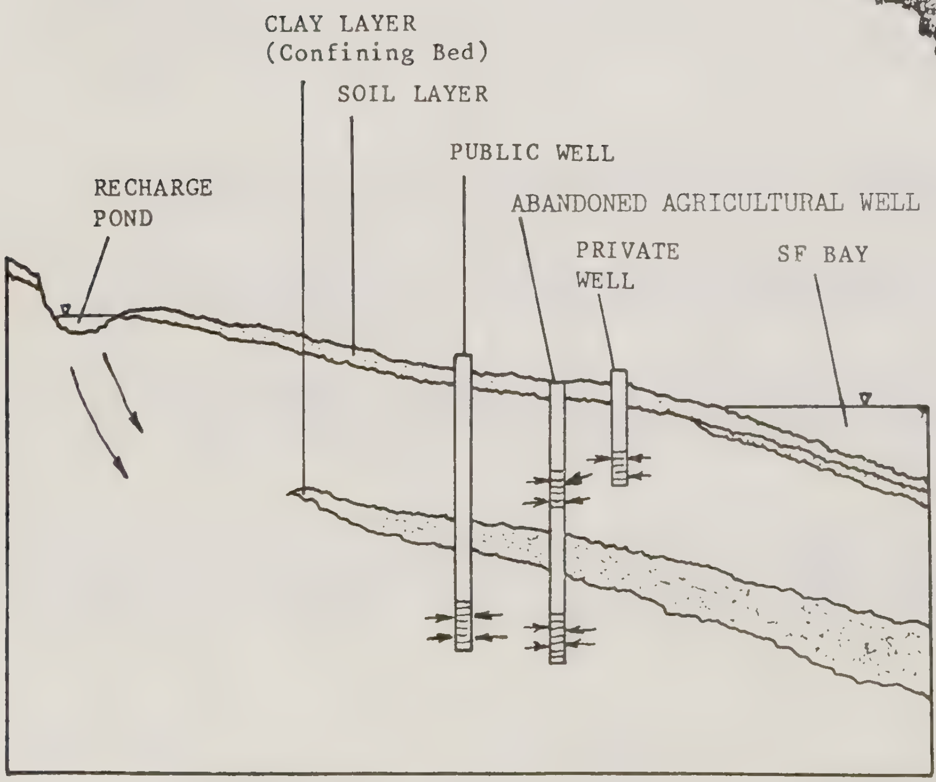

FIGURE 2

PERMITTING OF HAZARDOUS WASTE INCINERATORS IN CALIFORNIA

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ABSTRACT

Three hazardous waste incinerators have been issued a permit or variance from the California Department of Health Services in order to conduct a trial burn and allow limited operation. Several other incineration projects are at various stages of the permitting process, while some projects have been stopped or postponed indefinitely. There are many issues which have led to the success or failure of these projects. Among the key issues are: site location and physical geography, local opposition, waste analysis plans, trial burn plans and test results, safety and contingency plans, technical considerations, and requirements of local permitting agencies. A discussion of these details is presented.

Case histories are presented for the incineration permits or variances which have been issued to:

1. General Portland Cement Company, located in Lebec, California.
2. Stauffer Chemical Company, located in Carson, California.
3. GA Technologies, located in LaJolla, California.

Each case history includes a description of the project and incinerator, an account of the major obstacles that were addressed in the permitting process, a description of the trial burn and its results, and a discussion of the operating constraints contained in each of the permits. An overview of non-permitted hazardous waste incineration

PERMITTING OF HAZARDOUS WASTE INCINERATORS IN CALIFORNIA

INTRODUCTION

State and federal regulations, along with the liability associated with the land disposal of hazardous wastes, have spurred generators of these wastes to consider using more expensive and more environmentally sound hazardous waste disposal practices. Because incineration produces a much less toxic residual, the incineration of liquid organic hazardous wastes, when performed safely, is considered by many to be the most environmentally sound alternative to the land disposal of these wastes. These incentives have increased the demand for incineration facilities, however, there are several obstacles which have impeded the siting and permitting of commercial hazardous waste incineration facilities. Aside from the capital and economic considerations, the most significant obstacles to the permitting of a hazardous waste incinerator include: site location and physical geography, local opposition, trial burn plans and results, safety and contingency plans, other technical considerations, and requirements of local permitting agencies.

PERMITTING AGENCIES

In California, the permitting of a hazardous waste incineration facility is a very complicated process which includes the involvement of several different government agencies. Depending upon the scope of the project, an incineration facility may be required to obtain permits from: 1) the Environmental Protection Agency, 2) the California Department of Health Services, 3) the State Regional Water Quality Control Board, 4) the local Air Quality Management District, 5) the County Health Department, and 6) several other local and regulatory authorities. Of the aforementioned regulatory agencies, the State Regional Water Quality Control Board and the County Health Department usually have very limited and infrequent input into the permitting process, with this involvement usually being limited to technical review.

Depending upon the scope of the project, the incineration facility may be required to obtain both a RCRA and a TSCA permit from the EPA. The Toxic Substances Control Act (TSCA) governs the treatment and disposal of hazardous wastes containing polychlorinated biphenyl (PCB). Thus any incineration project which proposes to incinerate PCB must first obtain a TSCA permit. The TSCA contains performance requirements for the incineration of PCBs which include demonstration that the incinerator is

capable of a 99.9999 percent destruction and removal efficiency (DRE). Because of the political volatility of PCB issues and the additional permit requirements, most hazardous waste incineration proposals in California exclude the incineration of PCBs. Since any incineration project proposing to incinerate PCBs would most likely plan to burn other hazardous wastes, a RCRA permit would also be required.

The RCRA contains performance requirements for the incineration of hazardous wastes which include demonstration that the incinerator is capable of 99.99 percent DRE for the principle organic hazardous constituents (POHCs) introduced into the incinerator during a trial burn. POHCs and trial burn operating conditions are chosen so as to represent "worse case" conditions anticipated during normal operations. The results of the trial burn are used to determine compliance with the applicable destruction and performance requirements, as well as to assess the facility's overall environmental impact. These results are also used to determine operating conditions to be contained in the permit.

A hazardous waste incineration project can circumvent the RCRA permitting process and requirements by proposing to incinerate wastes as supplemental fuel, and to only burn wastes with a significant heat of combustion value. Two hazardous waste incinerators have avoided the RCRA permitting process by taking advantage of this exemption. However, by 1987 most types of incinerators and furnaces burning supplemental fuel will be required to obtain permits in much the same manner as hazardous waste incinerators which do not qualify for this exemption.

In California, the Department of Health Services (DHS) is the state agency with primary authority to regulate the management and disposal of hazardous wastes, and as such, has adopted regulations for the incineration of hazardous wastes. The incineration regulations are essentially identical to the requirements contained in RCRA, with the largest exception being that the DHS regulations do not exempt the incineration of hazardous wastes as supplemental fuel. Since the DHS incineration regulations are essentially identical to the RCRA requirements, to avoid duplication of efforts, the DHS is working in cooperation with EPA Region IX and is only performing minor review of incineration proposals which are required to obtain a RCRA permit.

The local Air Quality Management Districts have the authority to regulate sources of air pollution within their jurisdiction. As regulations vary from district to district, the obstacles that an incineration project must overcome in order to obtain a permit from the air quality management

districts is indeterminate. The local Air Quality Management Districts and the California Air Resources Board (CARB), developed regulatory guidelines specific to hazardous waste incineration. It should be noted that since most of the air districts within California are not in compliance with national ambient air quality standards, siting and permitting of a new hazardous waste incinerators usually involves obtaining emissions offsets and/or application of the best available control technology (BACT).

The involvement of local regulatory authorities, such as the city planning commission or the county board of supervisors, also varies widely from project location to location. Decisions made on this level are often times political in nature, and are often times greatly affected by the attitude and involvement of citizens within the political jurisdiction.

SUMMARY OF INCINERATION PROJECTS AND PROPOSALS

Within California there are several hazardous waste incineration projects at various stages of the permitting process. The majority of these projects are existing on-site incinerators for which the part B permit application process is completed, has begun, or will begin shortly. A summary of these existing on-site incinerators, including the incinerator type, is presented in Table I.

Presently, there are three existing incinerators in California which are undergoing the permitting process to be allowed to accept wastes from off-site on a commercial basis. A summary of these incineration projects is presented in Table II. The first and only facility which was permitted to accept hazardous wastes from off-site for incineration was the General Portland Cement Company located in Lebec, California. The company has a large rotary kiln which manufactures portland cement, and is exempt from obtaining a RCRA permit since the facility only accepts high BTU wastes to be burned as supplemental fuel. A second facility, Stauffer Chemical Company, in Carson California, is seeking both state and federal permits to accept hazardous wastes from off-site for incineration. In Carson, Stauffer Chemical Company owns and operates a liquid injection furnace used to regenerate and produce sulfuric acid. As with the General Portland facility, Stauffer Chemical Company's Carson facility will initially only accept wastes which can be burned as supplemental fuel, thus avoiding the RCRA part B permit process. The third facility attempting to be permitted to accept hazardous wastes from off-site for incineration is the GA Technologies facility located in LaJolla, California. At the LaJolla facility, GA Technologies owns and operates a pilot scale circulating fluidized bed incinerator. As a pilot scale incinerator, the facility is only permitted to accept small quantities of hazardous wastes to

demonstration the process to prospective clients. The facility is exempt from obtaining a RCRA permit since it does not accept hazardous wastes for disposal. However, the facility is obtaining a "Research, Development and Demonstration (RD&D)" permit from the EPA to allow continued testing of the incinerator. GA Technologies has previously received variances from the DHS in order to conduct trial burn testing and expects to obtain a variance permit from the DHS to allow testing in the future. A more detailed discussion of these permitted incineration projects is presented below.

Numerous incineration projects are in the planning and developmental stages, while other proposals have been abandoned altogether. A summary of these proposals and their status is presented in Table III.

OBSTACLES TO SITING AND PERMITTING OF INCINERATORS

SITE LOCATION AND PHYSICAL GEOGRAPHY

Site location and physical geography has influenced the siting and permitting of hazardous waste incineration projects. Site location is important for two reasons; the political climate in surrounding areas and the physical geology and of the site. There are several areas throughout California which are politically active and which have become very sensitive to pollution and hazardous waste issues as the result of previous spills, groundwater contamination, or waste management problems. An example of this is the large amount of local opposition to the Wolfskill-Anderson incineration proposal in the Riverside area. Residents of this area have become concerned with hazardous issues as the result of the highly publicized problems associated with the Stringfellow Landfill located nearby. Thus, the political climate of an area, and the proximity of the site location to residential areas have become major concerns of people wishing to site an incinerator.

The physical geology and geography has influenced the siting of several incineration proposals. One incineration proposal, which has been postponed indefinitely, proposed using a site which was within one quarter of a mile from the San Andreas fault, California's largest and most active earthquake fault. The location of a proposal to incinerate wastes as supplemental fuel in a cement kiln raised considerable concern because rainwater runoff from the facility and its surroundings flowed to a reservoir which supplies Stockton and portions of the San Joaquin Valley with drinking water. In addition to the aforementioned concerns, there are numerous other concerns such as proximity of residents and volume of wastes generated near the proposed site which must be taken into consideration when choosing a facility location.

TECHNICAL CONSIDERATIONS

Throughout the hazardous waste incinerator permitting process numerous technical considerations arise which must be addressed. These technical considerations arise during review of the Part B permit application and during development and approval of the trial burn plan. Problems frequently encountered during review of the Part B permit application include: 1) Waste analysis plans which are insufficient to characterize the possible components of a waste stream, 2) Safety and contingency plans which must be improved in order to protect employee and public safety, 3) The amount and type of air pollution control equipment required, and 4) The amount and type of emissions monitoring equipment for both airborne and waterborne emissions.

Additional technical considerations are encountered in the development of the trial burn plan. Although the number of agencies involved in the process can hinder progress, the large number of choices and issues which must be taken into account in developing a trial burn plan has been the cause of a considerable number of delays. Choosing the principle organic hazardous constituents (POHCs) for the test mixture, their respective feed rates, operating conditions, monitoring and sampling locations, sampling and analysis methods, and products of incomplete combustion (PICs) are among the decisions which must be made in developing a trial burn plan.

IMPOSITION OF LOCAL PERMITTING AGENCIES

Local permitting agencies and politicians are often times very responsive to the concerns, fears, and opposition to incineration projects from the people within their community. Although this opposition may not be founded in science, the threat of not being re-elected has persuaded several politicians to voice their opposition to local incineration projects even though they support the concept of hazardous waste incineration. A prime example of this involved a prominent State Senator. The senator has voted in support of, and has carried bills which support the expanded use of hazardous waste incinerators. When a project proponent proposed incinerating hazardous wastes as supplemental fuel at a site within the senator's jurisdiction, the incredibly large amount of local opposition persuaded the senator to publicly denounce the project based on technical considerations. Although the senator has no direct power regarding the permitting of a hazardous waste incineration facility, and local opposition doesn't usually reach into the state's political system, this type of response to public outcry is quite common on a local level. Since local opposition can be sufficient to kill a commercial incineration proposal,

management of the local opinion and opposition is of great importance in siting and permitting an incineration facility.

In attempt to address public opposition two different strategies have been used by project proponents. One strategy is to highly publicize the project, solicit public input and involvement, and to educate the local citizens and government officials of the benefits and relatively minor hazards associated with hazardous waste incineration. The second strategy involves walking quietly through the permitting, avoiding public involvement by only publicizing the project to the minimum extent required by regulations. Of these two strategies, the second has received much more success than the first. One reason for this is that in publicizing the project and trying to appear as a good corporate citizen within the community, project proponents have often times created and stirred up more opposition than if public involvement and participation was avoided. The incineration facilities which have been issued permits to commercially incinerate hazardous wastes have walked quietly through the permitting process and have encountered little or no opposition. None of the incineration proposals which have encountered considerable public opposition have received a permit as of this date.

CASE HISTORIES

GENERAL PORTLAND INC.

General Portland Inc. was the first company in California to receive a permit to incinerate hazardous organic wastes as supplemental fuel on a commercial basis. In 1982, the California Department of Health Services issued a temporary permit (6 months) to allow testing and limited operation of the facility. Testing was performed by the California Air Resources Board (CARB), and the facility has been issued successive short term permits to allow continued operation since that time.

General Portland Inc. operates a rotary cement kiln at their facility located in Lebec, a small town located in the high desert area of Kern County, California. The conventional rotary calciner dry process is used by General Portland at this facility, as opposed to either the wet process or preheater/precalciner systems in many other locations. The kiln is capable of temperatures which exceed 2500^{o}F and gas residence times on the order of 10 seconds.

Numerous tests have been performed on air emissions from the facility subsequent to initial permitting of the facility. Baseline tests were first conducted in order to determine background concentrations of

pollutants of concern. This was followed by tests of the incinerator while burning a waste solvent mixture which contained Freon 113, Dichloromethane, 1,1,1-Trichloroethane, Carbon Tetrachloride, Trichlorobenzene, and Toluene. Tests were also performed while simulating failure modes consisting of: 1) Turning off the air used for atomizing the waste into the kiln, 2) Having low excess oxygen concentrations in the furnace, and 3) Using a low BTU value fuel mixture. In addition, sampling and analysis of the following compounds was also performed: CO, NOX, SOX, HCl, Particulates, Total Hydrocarbons, Freon 11, Trichloromethane, Trichloroethene, Benzene, Polychlorinated Dibenzodioxins (Dioxins), and Polychlorinated Dibenzofurans.

The test results for organic compounds showed that at normal operating conditions, for almost all POHCs, the incinerator is capable of a 99.99 percent destruction and removal efficiency (DRE) as required by regulation. The one exception being that Dichloromethane appeared to have measured DRE of between 99.9 and 99.99 percent. However this data was acceptable to the regulatory authorities, as the actual DRE for Dichloromethane was indeterminate since the compound is also generated as a product of incomplete combustion (PIC) when burning the other compounds contained in the synthetic waste mixture. Dioxin and furan emissions were determined to be higher during background tests when burning only coke, than the emissions released during subsequent testing when the synthetic waste mixture was being fed into the incinerator. In addition, dioxin and furan emission concentrations were lower than compared to values reported in literature for municipal incinerators.

In attempting to obtain a permit, General Portland Inc. encountered numerous issues and concerns which delayed the permitting process. The permitting process, which took over two years, was primarily delayed not by local opposition, but by the numerous regulatory and technical issues that were raised in permitting the state's first commercial hazardous waste incineration facility. The facility's permit contains several operating constraints and conditions which limit the amount and type of wastes which can be incinerated at the facility. The major constraints include: the waste must contain less then 50 ppm PCB, less then 3 percent by weight chlorine, and greater then 8,000 BTU per pound heating value. In addition, the total amount of waste fed into the incinerator must comprise less then 25 percent of the total heating value fed into the incinerator, and monitored CO emissions must kept below specified limits.

STAUFFER CHEMICAL COMPANY

Stauffer Chemical Company operates a liquid injection sulfuric acid

regeneration furnace at its facility in Carson, California. The facility consists of two separate furnaces each of which operate at $1800^{\circ}F$, and have gas residence times within the furnace of greater then 3 seconds. Each furnace is equipped with a waste heat boiler, a spray scrubber, gas coolers, a wet electrostatic precipitator, gas drying towers, SO_2 to SO_3 converters, SO_3 absorption towers, and either an additional wet electrostatic precipitator or a brinks mist eliminator. A trial burn was conducted by CARB at the facility in February and March 1985. In order to develop the trial burn plan, a panel of experts in the fields of combustion, chemistry, kinetics, and emissions testing was formed. The panel recommendations were incorporated into the trial plan, wherein a synthetic waste mixture was chosen to test the incinerator's performance and DRE capabilities. The synthetic waste mixture consisted of carbon tetrachloride, trichloroethane, trichlorobenzene, and pentachlorophenol.

The incinerator was tested without the synthetic mixture in order to determine baseline emissions. Subsequently, the incinerator was tested using the synthetic mixture during normal operating conditions, and during two different failure modes. The two failure modes consisted of operating at low temperatures and operating with low excess oxygen.

Destruction and removal efficiencies for the compounds which comprised the synthetic mixture were shown to exceed 99.99 percent under all normal operating conditions and exceeded 99.9999 percent for some of the compounds. Removal efficiency of the hydrochloric acid generated from the combustion of these halogenated organic compounds exceeded 99.99 percent. Chlorinated dioxins and furans were sampled and analyzed, along with a number of other products of incomplete combustion. Analysis of the stack samples showed either very low (less than 2 ng/m^3 or undetectable dioxin and furan emissions rates.

Major obstacles which slowed and delayed the permitting process for Stauffer Chemical Company's Carson facility were primarily governmental and technical in nature. Review of the permit application and addressing its deficiencies, development of a trial burn plan, scheduling of test dates, analysis of samples, and compilation of results, added up to a considerable amount of time. Additional time was taken up in making improvements and changes to the facility which were necessary to meet regulatory requirements. These changes and improvements included building a hazardous waste storage area with secondary containment, installing new CO and oxygen monitoring systems, implementing new emergency shut down procedures, and installing of a platform on the stack to perform sampling during the trial burn.

As with General Portland, the permit issued to Stauffer Chemical Company contains constraints and operating conditions in order to ensure safe operation. Operating criteria include: wastes accepted for incineration must contain at least 5,000 BTU per pound; the wastes must contain less then 50 ppm PCB, and must contain less than 5 percent chlorine. The incinerator temperature must be maintained above 1,800 ^{o}F while incinerating wastes, and the CO and oxygen concentrations must be monitored and kept within specified limits.

GA TECHNOLOGIES

GA Technologies owns and operates a pilot scale circulating fluidized bed incinerator at its facility located in LaJolla, California. GA Technologies is engaged in the permitting process in which they expect to receive a "Research, Development and Demonstration (RD&D)" permit from EPA region IX. This RD&D permit will allow GA Technologies to accept small quantities of wastes from generators in order to allow continuous testing and demonstration of their incinerator. Prior to this time, GA Technologies has been issued either a short term permit, or variances, on a case by case basis in order to conduct specific trial burns. In addition to a trial burn conducted by the California Air Resources Board, a TSCA trial burn has been performed using PCB contaminated soil.

The circulating fluidized bed incinerator developed by GA Technologies is an outgrowth of the traditional fluidized bed combustion technology. In the circulating fluidized bed combustor (CBC), the bed solids are purposely carried out the top of the main combustor, collected by a cyclone, and returned to the bottom of the combustor. Operation in a circulating mode offers the advantage of greater fuel to combustion air ratios, as well as greater turbulence in the combustor and more surface area for reaction. This enhanced mixing of the bed solids allows the CBC unit to operate at lower temperatures (< 1600 ^{o}F) and shorter residence times (< 2 seconds) then conventional incinerators, while maintaining the 99.99 percent DRE required by regulations. Additionally, limestone is introduced into the combustor as part of the bed solids. The presence of this limestone offers the potential for enhanced removal of halogen and sulfur by reacting with these compounds and incorporating them into the solid phase.

CARB performed trial burn testing of the CBC unit in May of 1984. After baseline tests were conducted, a liquid waste mixture consisting of the following compounds as POHCs was introduced into the incinerator: Hexachlorobenzene, Trichlorotrifluoroethane (Freon 113), Carbon Tetrachloride, and Trichlorobenzene. These compounds were mixed in a

xylene matrix in proportions to produce a chlorine concentration of approximately one percent. Tests using the synthetic waste mixture were conducted under normal operating conditions and at low temperature conditions. These tests defined a lower temperature limit of about 1500 ^{o}F above which the CBC unit is able to meet 99.99 percent DRE for the compounds listed above. At normal operating conditions, the CBC unit showed greater then 99.9999 percent DRE for hexachlorobenzene.

Additionally, a TSCA trial burn was conducted for EPA's headquarters office. This TSCA trial burn was conducted using PCB contaminated soil, and PCB spiked (10,000 ppm) soil. Results of this trial burn showed that at a temperature of 1600 ^{o}F, and a 2 second residence time, the CBC unit is capable of 99.9999 percent DRE as required by TSCA regulations.

As with General Portland and Stauffer Chemical, the major obstacles which slowed the permitting process were primarily governmental and technical in nature. Since the facility does not intend incinerate large quantities of waste, and only intends to use the CBC unit in LaJolla for demonstration testing, the type, necessity, and requirements for permitting have been in question. Initial plans were to permit the facility or issue a variance on a test by test basis; however, practicality has called for the issuance of a long term permit.

NEW HAZARDOUS WASTE INCINERATION FACILITY PROPOSALS

Numerous individuals and companies have approached the DHS and the EPA with ideas for constructing hazardous waste incinerators. The vast majority of these proposals die in the development stages when the project proponent discovers the large amount of work and capital required to develop the project with no guarantee that the incinerator will be issued a permit. A list of proposals which have proceeded beyond the idea stage are listed in Table III.

Of these new incineration facility proposals, the one by Chemical Waste Management has been postponed by the company. Local opposition has delayed or killed the proposals from Genstar Cement Company, Omega Chemical Company, and the Wolfskill-Anderson Recycling Center. Regulatory issues have slowed progress on the In-Process Technology proposal. Three new proposals which have been delayed only slightly, and are proceeding as planned are the Security Environmental Systems' proposal to site a rotary kiln in Vernon, the Stauffer Chemical Company's proposal to incinerate RCRA hazardous wastes in their liquid injection sulfuric acid furnace in Martinez, and Dow Chemical Company's proposal for a new rotary kiln in Pittsburg.

Table I

ON-SITE INCINERATORS IN CALIFORNIA

COMPANY	LOCATION	TYPE OF INCINERATOR	WASTES INCINERATED
ALPHA RESINS	PERRIS	LIQUID AND VAPOR INJECTION	ALDEHYDE VAPORS AQUEOUS PHENOL SOLUTION
ASHLAND CHEMICAL	LOS ANGELES	LIQUID INJECTION	RESIN RINSE WATERS
CARGILL	LYNWOOD	FIXED HEARTH	RESIN RINSE WATERS
CHEVRON CHEMICAL CO.	RICHMOND	LIQUID INJECTION	90% ORGANICS IN WATER
DOW CHEMICAL	PITTSBURG	LIQUID INJECTION THERMAL OXIDIZER	CHLORINATED STILL-BOTTOMS
IT VINE HILL	MARTINEZ	LIQUID AND VAPOR INJECTION	ORGANIC LIQUID AND VAPORS
LAWRENCE LIVERMORE	LIVERMORE	FIXED HEARTH	LIQUID SOLVENTS PATHOLOGICAL WASTES
SHELL OIL COMPANY	MARTINEZ	CO BOILER	ORGANIC SLUDGE HYDROCARBON LIQUIDS
SIERRA ARMY DEPOT	HERLONG	ROTARY KILN	NITROGLYCERINE ORGANO-METALS

TABLE II

OFF-SITE HAZARDOUS WASTE INCINERATORS

COMPANY	LOCATION	TYPE OF INCINERATOR
GENERAL PORTLAND INC.	LEBEC	ROTARY KILN
STAUFFER CHEMICAL COMPANY	CARSON	LIQUID INJECTION
GA TECHNOLOGIES	LAJOLLA	CIRCULATING FLUIDIZED BED

TABLE III

NEW INCINERATION FACILITY PROPOSALS

COMPANY	LOCATION	TYPE OF INCINERATOR	PROPOSAL STATUS
CHEMICAL WASTE MANAGEMENT	KETTLEMAN HILLS	ROTARY KILN	PROPONENT HAS HELD MEETINGS WITH DHS AND EPA. PROPONENT IS ANALYZING MARKET BEFORE PROCEEDING.
DOW CHEMICAL	PITTSBURG	ROTARY KILN	AFTER MEETING WITH DHS AND EPA, PROPONENT IS WAITING ON PROJECT.
GENSTAR CEMENT COMPANY	SAN ANDREAS	ROTARY CEMENT KILN	INITIAL PROPOSAL TO BURN PCB WAS ABANDONED DUE TO LOCAL OPPOSITION. PROPONENT IS PROCEEDING WITH NEW PROPOSAL TO BURN LOW TOXICITY WASTES AS SUPPLEMENTAL FUEL
IN-PROCESS TECHNOLOGY	PALO ALTO	THERMAL DECOMPOSITION UNIT	PROPONENT CLAIMS UNIT IS NOT AN "INCINERATOR" PER DEFINITION AND THEREFORE REGULATIONS DO NOT APPLY. DECISION HAS NOT BEEN FINALIZED.
OMEGA CHEMICAL	IRWINDALE	GA TECHNOLOGIES CIRCULATING BED COMBUSTOR OR ROTARY KILN	SEVERAL DIFFERENT SITE LOCATIONS HAVE BEEN PROPOSED. FIRST LOCATION ABANDONED DUE TO LOCAL OPPOSITION. SECOND LOCATION DUE TO LAND ACQUISITION. THIRD PROPOSAL IS IN VERNON

TABLE III (continued)

NEW INCINERATION FACILITY PROPOSALS

COMPANY	LOCATION	TYPE OF INCINERATOR	PROPOSAL STATUS
SECURITY ENVIRONMENTAL SYSTEMS	VERNON	ROTARY KILN	PROPONENT HAS COMPLETED PERMIT APPLICATION WHICH IS UNDERGOING REGULATORY REVIEW. PROJECT IS GOING AS PLANNED.
STAUFFER CHEMICAL COMPANY	MARTINEZ	LIQUID INJECTION	PROPONENT HAS APPLIED FOR A RCRA PERMIT TO BURN WASTE AT ITS MARTINEZ FACILITY. APPLICATION IS COMPLETE AND UNDERGOING TECHNICAL REVIEW.
WOLFSKILL-ANDERSON RECYCLING CENTER	RIVERSIDE COUNTY	CIRCULATING BED COMBUSTOR	PROPOSAL ENCOUNTERING CONSIDERABLE LOCAL OPPOSITION. STATUS IS INDETERMINATE.

COORDINATING HAZARDOUS MATERIALS TRAINING PROGRAMS

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THE HAZMAT TRAINING PROBLEM

Hazardous and toxic materials pose one of the foremost challenges of the eighties. Last year, over 1,610 hazardous materials incidents or spills were reported to the State, an average of one every six hours, every day of the year. The release of a toxic gas in Bhopal, India, demonstrated the scale of the problem which this type of disaster can represent; recent releases show that it can happen here. There are over 200 materials in use in California which are capable of causing a Bhopal-type incident.

As disasters, events involving hazardous materials pose unique problems. The agent itself is often hard to identify; the first people called to the scene are frequently police or fire employees who may not be sufficiently trained to analyze complex chemicals or evaluate appropriate responses. Swift protective action or evacuation of citizens is often imperative, yet these activities require efficient use of time and resources which call for advance coordination. Inappropriate response leads to increased deaths and injuries and legal liability of both government agencies and responsible employees.

Management of major emergencies is a complex and multi-disciplinary task, with the potential of involving nearly every element of the public sector, as well as private industry. Hazardous materials incidents may occur by themselves, or be a secondary hazard in another disaster such as an earthquake, fire or flood. The potential exists for both acute events, such as a sudden release either in air, water or the ground; or more chronic problems which develop and continue over a period of years.

A recent statewide survey conducted by CSTI to determine emergency management training needs in the State of California showed hazardous materials to be second only to earthquakes and then by less than a quarter of a percent. This need held constant in rural areas, where agricultural chemicals prevail; and in the urban parts of the state, where manufacturing and industry create and use potentially hazardous chemicals. The demand was strong among all disciplines surveyed, including fire servcies, law

enforcement, medical, schools and universities, state agencies and private industry personnel. The survey also revealed the need for hazardous materials training among the vertical levels of these organizations: from response personnel to supervisors or scene managers, through midlevel and top management to policy makers.

Probably the most difficult disaster response operation is a mass evacuation, and the largest of these yet accomplished was in response to a hazardous materials incident in Mississigua, Canada. At the same time, emergency managers must be prepared to use judgement and discretion, and not unduly expose the population to peril by imposing an unwise evacuation through a toxic substance.

CURRENT PROGRAMS

Gradual recognition of the problems of technological hazards has resulted in strong initiatives by the executive, legislative and judicial branches of government at both the State and Federal level. While attempting responsible actions, these various initiatives have led to fragmented, uncoordinated and duplicative efforts in some areas: one of these is training.

An extensive study by the Association of Bay Area Governments last year revealed hundreds of training programs under way nationwide. The California Specialized Training Institute just completed an update of the ABAG study in California, and discovered that some of the programs were very transitory, having been offered only once, while others have grown and expanded. We were able to confirm thirty-eight separate courses currently provided in California, by a variety of private, local, state and federal agencies; for a variety of disciplines and levels of personnel. A conscientious training manager currently has a tremendous challenge in selecting the appropriate training course or courses to which to send their personnel.

Another current problem is a lack of coordination among these training programs. There are certain things that fire service personnel need to know, others for law enforcement, health services, transportation, district attorneys, etc. Some discipline-specific courses provide excellent information for that discipline, but fail to cover what other disciplines at the site will be doing. Some courses aimed at "first responders" stress the Incident Command System, others fail to mention it. Because programs have tended to develop around funding sources, some disciplines are well trained while others have been neglected entirely. Some supervisors, managers and policy makers have not even been exposed to the concepts of operation in which their subordinates have been trained.

THE MULTIDISCIPLINARY APPROACH

The problems of current training programs have been recognized in several studies and research reports, including one by the California Auditor General.

Although no formal coordination has yet been established, dedicated individuals have shown great initiative in working together to meet training needs. For example, one recent training course was sponsored by the California Department of Health Services, conducted by a private contractor to the Environmental Protection Agency, located at the California Specialized Training Institute, with student expenses paid by the Federal Emergency Management Agency administered by the Office of Emergency Services!

Informal groups, such as the Emergency Response Coordinating Committee, have made limited progress through a lack of authority to make decisions. Sensitivities of "turf" and "territory" have prevailed.

The California Specialized Training Institute has conducted emergency management training since 1971, and has focused on hazardous materials management in special programs since 1978. We assisted with the development of the "Hazmat Module One" course and trained-the-trainers in 1980. We have participated in many task forces and coordination efforts through the years. Since we became the training arm of the state Office of Emergency Services, in 1985, these coordination efforts have intensified. However, we are hampered, like others, by a lack of resources, both personnel and financial, to thoroughly address the coordination issue. We also, like others, lack the authority or mandate to successfully direct the statewide training effort.

LEGISLATIVE INITIATIVES

At least two bills are under consideration by the legislature to address the hazardous materials training coordination issue. One, AB2702 by Assemblywoman LaFollette, places OES, specifically CSTI, in the lead role. It establishes a Curriculum Advisory Group with wide representation, and provides personnel and financial resources to adequately meet this challenge. Another, AB2657 by Assemblyman Elder, charges the Department of Health Services with similar responsibilities.

At the date of this writing, the Governor has not taken an official position on either bill, nor have hearings been held in the legislature. However, the attention given this issue by the legislature, the media and the public at large will probably catalyze

the efforts of training providers in the state to organize and coordinate.

The California Specialized Training Institute looks forward to participating in whatever coordination effort emerges. Our long association with the many disciplines involved in emergency management will be reflected in our approach to training coordination. We know you seek programs which deliver the technical and management training needed for your discipline, as well as a respect and understanding of the other disciplines involved in these incidents. To the best of our abilities we will seek to see that training programs offered will meet those needs.

HOW TO WRITE AN ENFORCEABLE HAZARDOUS MATERIALS ORDINANCE

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INTRODUCTION

Handouts

Three handouts will be available at the May 1, 1986, 1:30 p.m. session ("Local Programs and Regulations"): Handout #1 is a model minimum ordinance which cities or counties might use either to "implement" AB2185 or to create a disclosure ordinance of their own. Handout #2 is a model minimum ordinance for regulating underground tanks. Each model ordinance contains a cover sheet with comments. Handout #3 contains a list of periodicals and books dealing with legislative drafting and California hazardous materials law, and a list of the state agencies that administer hazardous materials law.

Author's Background

The advice in this paper is a result of my participating from October, 1985, to the present as a volunteer legal advisor to the Implementation (drafting) Subcommittee of San Francisco's Hazardous Materials Advisory Committee (HMAC). The HMAC is a citizens group, appointed by the Board of Supervisors, which is responsible for proposing revisions to San Francisco's current Hazardous Materials Permit and Disclosure Ordinance, first enacted in December, 1983.

Intended Audience

I have written this paper for county and city employees and other persons (including lawyers) who have little or no experience in legislative drafting or who know little about hazardous materials, hazardous waste, or environmental law, but who might be called upon to draft or review some kind of hazardous materials ordinance. I assume an ability on the part of the draftsperson to perform minimal legal research among state statutes and county/city municipal codes.

Major Types of Hazardous Materials Ordinances

Most California hazardous material ordinances deal with four topics: (1) disclosure of the use of hazardous

materials (this disclosure is now required by AB2185, enacted in 1985 by the California legislature); (2) regulation of underground tanks (also required by California statute); (3) accidental release or clean-up of hazardous materials; and (4) a new phenomenon related to land use and zoning - a requirement that real estate developers test for hazardous materials before they obtain a building permit. I discuss in this paper only (1) and (2).

HOW CAN COUNTIES AND CITIES "IMPLEMENT" THE STATE-MANDATED PROGRAMS?

Both AB2185 and the state underground tank statute require counties and cities to "implement" state law except in certain circumstances. However, neither AB2185 nor the underground tank statute define "implementation" or describe how counties and cities are to implement the state-mandated programs. There are also no state regulations under either statute that deal with implementation. The State's lack of guidelines in probably intended to allow localities a variety of implementation methods. In any case, local legislation is certainly only part of "implementation."

Do You Need An Ordinance?

At this late date (May 1, 1986) there is no need for counties or cities to create from scratch a hazardous materials disclosure ordinance or an underground tank ordinance, because the State of California has in a sense provided them with models, i.e., the language in AB2185 and in the state statute on underground tanks. (I created Handout #1 and Handout #2 by using these two statutes as a guide.) If your county/city wants any other type of hazardous materials ordinance, you'll probably have to create it without any prior models.

AB2185 - State Requirements For Implementation

AB2185 (Waters), which became effective January 1, 1986, is codified in California Health and Safety Code Sections 25500-25521. Note a few things about AB2185: (1) It is only a disclosure statute. (2) AB2185 does not regulate counties or cities themselves (as opposed to the state law of underground tanks, which requires regulation of municipally-owned underground tanks). AB2185 requires only businesses to provide information about the hazardous materials they use or store. (However, counties and cities must create an "area plan" for hazardous materials emergencies.)

AB2185 - Counties

There is no need for a county to have any ordinance at all in order to "implement" AB2185. All that AB2185 requires is that counties somehow "implement" the state program. California Health & Safety Code § 25502(a).

Any county which "implements" the state program (whether or not the county has enacted an ordinance of its own to do so) must by implication implement a disclosure program in those cities that are not exempt from AB2185 by virtue of having a disclosure program of their own. California Health & Safety Code § 25502.

AB2185 requires all counties, and those cities that have their own program (which city program must be enacted by an ordinance), to notify the California Office of Emergency Services of the identity of the county/city "administering agency." California Health & Safety Code § 25502(c). However, it might be appropriate for a county/city to have its "administering agency" adopt some regulations publishing the requirements of AB2185 or its own program, in order to avoid a legal challenge by a regulated business that the county/ city is acting arbitrarily in imposing a certain requirement.

AB2185 - Cities

Cities may either (1) choose to let the county dictate what program the city must have; (2) enact an ordinance creating their own disclosure program, which must be at least as strict as AB2815 (thereby avoiding county control); or (3) "by ordinance, assume responsibility" for implementing AB2185. California Health & Safety Code § 25502(b).

AB2185 contains no deadline by which cities are required to have enacted an implementing ordinance, but it does contain a November 1, 1986 deadline by which businesses are to have submitted "business plans" to the city's "administering agency." Therefore, practically speaking, a city must have enacted its ordinance well before November 1, 1986. California Health and Safety Code §25505.

AB2185 - Minimum Possible Ordinance for Counties and Cities

If a county or city chooses to write an ordinance that either creates the county's/city's own disclosure program or "implements" the state program, that ordinance must obviously contain certain minimum provisions. My version of a "bare bones" minimum disclosure ordinance (which counties or cities could use to create their own program or use as part

of its AB2185 implementation) is contained in Handout #1. You might want to add to it.

Underground Tanks - State Requirements For "Implementation"

Theoretically, it is too late now for either a county or city to write an ordinance to create an underground tank regulatory program of its own. However, a county or city could still enact an ordinance in order to "implement" the state program, although enacting an ordinance is merely one phase of "implementing" the state law.

The state statute on underground tanks, which became effective on January 1, 1984, is codified, as amended, in California Health and Safety Code §25280 - 25299.6. The statute requires all counties to "implement" the law "pursuant to regulations adopted by" the State Water Resources Control Board. California Health & Safety Code § 25283. The State Water Resources Control Board did not adopt regulations until August 13, 1985. The Board's regulations have never defined "implementation."

Underground Tanks - Counties

A county was entitled to an exemption from this requirement to implement the state program only if:

(a) before January 1, 1984 the county had an ordinance which at least met the requirements of Health and Safety Code Sections 25284 and 25284.1 as they read on January 1, 1984 and (b) any subsequent amendments to the county ordinance have continued to meet the requirements of 25284 and 25284.1 as they read on January 1, 1984. California Health & Safety Code § 25299.1.

As part of implementing the state underground tank program, the State Water Resources Control Board informally requires counties to take some sort of "formal" action, e.g., a resolution by the board of supervisors, although no formality is actually required either by the underground tank statute or by the state underground tank regulations contained in Title 23, California Administrative Code Sections 2610, et seq.

Any county-wide program must by implication be implemented in those cities within the county that are not exempt by virtue of having created their own program or by virtue of having adopted the state program by ordinance. Counties that have written underground tank ordinances or developed regulations or adopted a resolution might want to include in them an explicit statement imposing the county program on

non-exempt cities within the county, in effect forcing the cities to implement the county program.

Note that the state underground tank statute does regulate underground tanks owned or operated by counties and cities, in comparison to AB2185 which does not require counties or cities which use or store hazardous materials to provide to the county or city "administering agency" the same information which businesses must provide.

Underground Tanks - Cities

Cities are now governed by a county's implementation plan or the county's own program unless:

(1) the city "assume[d] responsibility for the implementation" of state law before January 1, 1986. (The only method by which a city could have assumed this responsibility was to write an ordinance, California Health & Safety Code § 25283), or

(2) (a) before January 1, 1984 the city had an ordinance which met the requirements of Health and Safety Code Sections 25284 and 25284.1 as they read on January 1, 1984 and (b) any amendments to the city ordinance have continued to meet the requirements of 25284 and 25284.1 as they read on January 1, 1984.

Underground Tanks - County Non-Compliance

On March 13, 1986, I learned from the State Water Resources Control Board that several counties are "dragging their feet," i.e., they are not implementing the state law (whether or not they have their own ordinance). This means that these counties are in violation of the state statute. These counties are mostly the smaller "contract counties", so-called because they contract with the California Department of Health Services to provide these counties with a sanitarian. Some of these counties try to get the contract sanitarian to conduct the county's state-mandated underground tank program (for example, by issuing underground tank permits and collecting permit fees). However, this type of work is not in a sanitarian's area of expertise.

Although the state statute regulating underground tanks contains no penalty provisions for counties that are not implementing the state law, it seems possible to me that eventually the State Water Resources Control Board or some other state agency might attempt to impose some sort of sanction on these counties. In addition, any accident which occurs as a result of a county's not having "implemented"

the state underground tank program exposes the county to liability.

LOCAL IMPLEMENTING LEGISLATION

Delegation

Many, if not most, county and city charters explicitly state that all municipal powers are to be exercised by the local governing body, i.e., a board of supervisors or a city council. Moreover, California Government Code §23005 requires a county to exercise its powers only through the board of supervisors or agents acting under the authority of the board. Thus, if the county or city does not delegate the responsibility to implement a state-mandated program, the responsibility remains with the local governing body. Therefore, some kind of formal delegation of responsibility will almost always be necessary.

Note also that a county or city charter might require that all legislative acts must be done by means of an ordinance, thereby eliminating some of the options below.

Possible Forms of Local Legislation

California Government Code Section 50022.2 permits counties and cities to adopt state statutes and county ordinances, respectively, by reference.

1. A county or city could enact an ordinance adopting verbatim the state statute *in toto*. As to AB2185, such an ordinance might be worded as follows: "The County of ____________ adopts the state law of hazardous materials disclosure contained in California Health and Safety Code Sections 25500-25521, to be effective immediately. The County Department of ______________ is hereby authorized to implement the state law and adopt regulations reasonably necessary to implement the state law." For the exact language required in all county ordinances, see California Government Code §25120.

This method leaves much to be desired, because (1) the state law contains many provisions that are *irrelevant* to local implementation. It also confuses citizens who must comply with, and local government officials who must enforce, state law, since they must always check to see whether the local regulations conflict with the state statute.

2. A county or city could adopt *selected* portions of the state statute: "The County of __________ enacts the state law of hazardous materials disclosure contained in California Health and Safety Code Sections 25500-25521 by

adopting the following sections of the state law as its own: Section __________, Section ___________, Section ____________."

This method also leaves much to be desired, because even individual provisions of a state statute often contain regulatory <u>options</u> which a county <u>may</u> use, but does not specify them. In addition, the same considerations as in 1. above apply.

3. A county or city could merely adopt a <u>resolution</u> stating that a certain county/city department is authorized to implement the state program by adopting any necessary regulations and adding any regulations it considers desirable to add further protection for the public. (Note that such a resolution is probably a "legislative action" within the meaning of many city charters and would therefore require the mayor's signature.)

4. A county or city could write its own ordinance by using the model minimum ordinances I have provided in Handout #1 or #2, adding any provisions considered desirable, and is supplementing it with local regulations.

5. A county or city could create its own ordinance from scratch, but I do not recommend this method. Why reinvent the wheel?

<u>How Much Should You Include In One Ordinance</u>?

Since state law requires two programs to be implemented (AB2185 and the underground tank law) you could write one ordinance that satisfies both AB21815 and the underground tank law. I recommend against this for the following reasons.

The <u>advantage</u> I see is that you would need only one common set of definitions. The <u>disadvantages</u> I see are:

(1) AB2185 requires counties/cities to implement only a <u>disclosure</u> (information-gathering) program and create an "area plan."

Because AB2185's definition of "hazardous material" includes hazardous waste, if a county/city attempts to regulate above-ground hazardous materials, it could inadvertently fail to distinguish between above-ground hazardous materials and above-ground hazardous waste. In my opinion, any attempt by a county or city to regulate above-ground hazardous waste without having been designated as a state enforcement agency pursuant to California Health and Safety Code Section 25180 would be declared invalid, because the

state already has its own extensive regulatory program for hazardous waste and has therefore preempted this area of above ground hazardous waste regulation, except where state statutes explicitly state or obviously demonstrate an intent not to preempt local regulations, as in the state law of underground tanks.

By including, in one ordinance, provisions for regulating underground tanks (where the state allows localities to regulate hazardous waste by virtue of the definition of "hazardous materials" in the state statute dealing with underground tanks) and provisions related to disclosure of above-ground "hazardous materials" (which include "hazardous waste"), you run the risk of thinking you can dictate to a business how it must store or handle above-ground hazardous waste when you are authorized by state law only to require information from businesses that store or handle hazardous waste.

(2) If a county/city designates one department to implement the AB2185-related (disclosure) portion of the ordinance, and another department to implement the underground tank portion, the chance of error in drafting or revising the ordinance increases if neither department is familiar with the other portion of the ordinance.

FEES AND PERMITS

If counties/cities want to charge fees in connection with implementing AB2185 or the state underground tank program, you will probably have to have at least an ordinance setting fees, unless you already included fee provisions in a disclosure ordinance or underground tank ordinance. Although California law in general does not require counties and cities to adopt ordinances in order to charge fees (they could, for example, be set by a local department's regulation or by other means), both AB2185 and the state underground tank law explicitly allow counties and cities to charge fees for implementing the state programs if the county/city enacts a fee ordinance. Thus, it would appear that if you don't enact such an ordinance, you may not charge fees. (Note that both AB2185 and the state underground tank law specify that the fees may be only enough to conduct the implementation program. This is merely a restatement of the California case law regarding the right of municipalities to charge fees.)

If you are conducting your own program rather than a state program (and are therefore not subject to State law), whether an ordinance setting fees is required depends on your local law.

Although owners and operators of underground tanks must obtain permits from the county/city, AB2185 does not have a similar requirement. It might be advisable not to issue a document called a "permit" in connection with AB2185; that way you avoid the risk of thinking that AB2185 authorizes localities to regulate storage of above-ground hazardous waste.

OVERVIEW OF LEGISLATIVE PROCESS

The steps are: (1) Plan; (2) Draft (outline, write, review, revise); (3) Implement; (4) Enforce; and (5) Amend. I discuss below only (1) Planning and (2) Drafting.

PLANNING

Knowledge Required of the Draftsperson

You should have a minimum knowledge of the relevant state statutes and state regulations before or soon after you begin planning. Familiarize yourself with the following:

1. AB2185 (California Health and Safety Code Sections 25500-25521) and proposed regulations (see Handout #3);

2. the state law of underground tanks (California Health and Safety Code Sections 25280-25299.6) and state regulations (Title 23, California Administrative Code, Sections 2610, et seq.); and

3. the state law of hazardous waste control (California Health and Safety Code Sections 25100-25242.3) and state regulations (Title 22, California Administrative Code, Sections 66000 et seq.).

Note also that 1985 state legislation (California Health and Safety Code Section 212) requires the California Department of Health Services to publish a compilation of all California laws dealing with hazardous materials and hazardous waste. This has not yet been published (see Handout #3).

Investigate What Has Been Done Before

Examine ordinances from other counties or cities; for example, the Santa Clara County ordinance and the San Jose City ordinance. Both of these ordinances, however, attempt to combine the disclosure (information-gathering) required by AB2185 with the regulation of underground tanks (and both of them in my opinion run the risk of a preemption challenge

if they are used to regulate above-ground storage of hazardous waste).

Check For Conflicts With Other Ordinances

Determine whether your proposed ordinance will overlap or conflict with other ordinances in same county/city. You should scan all municipal codes that might be related: fire code, health code, and those which deal with permits, fees, and permit appeals. Certain municipal code sections might already regulate non-toxic hazardous materials (e.g., fireworks) and underground tanks, or set inspection/permit fees. Decide whether you will need additional local legislation to amend these other codes.

Determine which county/city department(s) will enforce the ordinance.

This must be decided for you. It is crucial to have this decided as soon as possible!

Talk to the department chiefs (or his or her staff members) in the department(s) that will enforce the ordinance.

Get the department chief(s) to indicate (in writing, if possible) what the county/city local "implementation" program (or its own program) will consist of, and what will be included in the ordinance. By "chief" I mean the highest ranking official, e.g., the Director of Public Health or the Chief of the fire department.

Department chiefs probably will not not know the law of hazardous materials or the law of underground tanks. If so, locate and talk to staff members in these departments who do have expertise. Ask the staff members what type of program they think the department chief(s) would want.

You could also give the department chief(s) or staff a copy of AB2185 and the state tank law, as well as similar ordinances from other localities, in order to let them know the issues that are involved. If neither the department chiefs nor staff members have expertise, have them talk to experts from other localities. You might be able to organize a small conference of experts to talk with the department chiefs or staff members.

You could also talk to the other local experts yourself and then report back to the chief.

If more than one county/city department will be involved in implementing the program or enforcing the ordinance, disagreements between departments can arise.

Discover these areas of disagreement early. For example, if more than one department must approve a permit, each department might require its own inspection. This requirement for two inspections will affect the implementation program budget (manpower and permit fees).

Make sure that the staff of both departments participate, that they talk to their department heads, and that the department heads talk to each other. Early!

During all this planning activity, document the dates of your communications and other activities. These days hazardous material is a "hot topic": When the news media start investigating, governmental officials look for scapegoats.

During the planning stage discuss with the implementing department(s) the legal issues mentioned on page 12. For example, someone must decide whether county/city departments will be subject to AB2185 disclosure requirements, and if so, whether these departments will have to pay a fee.

Budget Considerations

Any county/city program to implement required state programs is going to require people, and, therefore, money. Someone will probably have to submit a budget proposal to the local legislative body.

DRAFTING (Writing)

One person should write the entire ordinance and at least one other person (preferably a lawyer) should review it. I recommend that a lawyer perform the final review of the ordinance before it is enacted, because lawyers will usually be the most perceptive critics of the ordinance. Here the most helpful attitude the lawyer can take is that of a possible adversary advising a client how to comply with the ordinance.

A possible way to compensate in the planning stage for the draftsperson's lack of expertise in hazardous materials is to use a small advisory committee whose members do have the expertise. Such a committee might be of great help in planning, but writing an ordinance is not a group effort. Note also that now there is state legislation to guide you; the need for a committee is not as great as it was a few years ago.

DRAFTING (Legal Review)

Following is a brief description of some of the major legal issues involved in hazardous materials ordinances. Keep these in mind when you review the ordinance. You should also consider these issues during the planning phase. I will elaborate on the issues below at the May 1, 1986 HAZMACON '86, 1:30 p.m. session ("Local Programs and Regulations").

Preemption by state law

Local disclosure (i.e., AB2185-type) programs must contain requirements at least as strict as AB2185 itself (i.e., the same or greater disclosure standards).

Local regulation of transportation of hazardous materials through counties/cities is almost totally preempted by state law. Counties and cities may regulate in this area only in a limited manner.

Labeling requirements for hazardous materials are preempted by state law. See the discussion on pages 7-8, above.

Local regulation of the storage of hazardous waste above ground is, in my opinion, likely to be declared by a court (in the event of a legal challenge) as preempted by state law.

If state law prescribes criminal sanctions for certain violations of state law, counties and cities may not impose different penalties.

Constitutionality (Due Process)

A denial of certain privileges (e.g., revocation of a permit) will require notice to, and a hearing for, the regulated person or business.

Overly vague definitions of key terms in an ordinance or regulation might invalidate it for not providing adequate notice of what is required of the regulated person or entity. This consideration is especially important in situations where regulated persons or businesses are subject to criminal sanctions, as they are, for instance, under AB2185 and the state underground tank law.

An ordinance which purports to make "any violation" a criminal violation without specifying which violations in particular subject a person to criminal sanctions are almost certain to be declared unconstitutionally vague by a court.

Promulgating Regulations

California law does not require counties or cities to follow any particular procedure in adopting local regulations. However, some county and city charters or ordinances do have such requirements, e.g., the necessity for a public hearing by the department adopting the regulations.

No regulation may alter, amend, or conflict with the local ordinance under whose authority the regulations were adopted.

Limiting a county's/city's liability

Some ordinances attempt to absolve a county or city from liability for negligent enforcement or non-enforcement of state-mandated duties. Such an attempt is futile, because in California the liability of governmental entities is completely governed by state statute. See California Government Code Sections 810, et seq., and the cases interpreting these code sections.

Fees

Any fees charged by a county/city for conducting a disclosure program or underground tank program must be reasonably related to the cost of conducting the program.

You cannot impose a county/city fee on one class of persons or businesses (for example, a charge of $50 on all gasoline stations) to support a program that regulates other class of persons or business (for example, all businesses using underground tanks).

Your county or city might already have enacted general ordinances specifying the procedure for collecting permit fees.

Inspections

AB2185 and some local underground tank programs require inspections of hazardous materials facilities, and AB2185 and the state statute on underground tanks impose criminal sanctions for certain violations. Therefore, a search warrant signed by a magistrate will probably be required if a person refuses to let the county/city conduct an unannounced inspection.

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IMPLEMENTING LOCAL HAZARDOUS MATERIALS STORAGE ORDINANCES: THE SANTA CLARA COUNTY EXPERIENCE

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INTRODUCTION

Silicon Valley, which occupies much of California's Santa Clara County, is the birthplace of the computer-based information age. Appropriately enough, it is also the birthplace of local government regulation of hazardous materials and hazardous wastes, including those produced by the computer industry. In 1983, Santa Clara County and its fifteen constituent cities began to implement Hazardous Materials Storage Ordinances (HMSOs), based on a model ordinance developed within the county. The model ordinance was developed through the concerted efforts of city managers, fire departments, and business and environmental representatives working on a task force under the overall aegis of the county-wide Intergovernmental Council (IGC). The model ordinance presents a uniform approach to both underground and above ground storage of hazardous materials (hazmat) across the county's sixteen jurisdictions, for the benefit of both regulators and business.

Regulation of hazmat storage is now recognized as a powerful environmental protection tool. California adopted a statewide law regulating underground storage in 1983 (AB1362), based on the Santa Clara County model. The Federal Resource Conservation and Recovery Act (RCRA) amendments of 1984 extended this underground tank program nationwide; EPA is now drafting national regulations. New California law (AB2185) will require statewide attention to above-ground storage in 1986. Proposed amendments to the Federal Superfund Law (CERCLA), now pending in Congress, would mandate similar controls nationally.

What lessons can be learned from HMSO implementation? As agencies around the country brace for implementation of laws governing underground and above ground storage, the Santa Clara County experience can provide useful guidance. The remainder of this paper describes the history of HMSO implementation, identifying issues that will probably arise elsewhere.

CREATING THE MODEL ORDINANCE

The Santa Clara County model HMSO was developed in 1982-1983 by a task force including participants from local government, industry and environmental groups. The Santa Clara County Fire Chiefs' Association sponsored the effort, because of firemen's need to know the location and content of above ground hazmat storage facilities when responding to emergencies. The firemen were joined by a broad range of groups also concerned that leaks from both above ground and underground tanks would contaminate the aquifers from which half of the county's drinking water is drawn; major leaks at IBM and Fairchild plants in south San Jose in 1981 focused public attention on this problem.

The task force mechanism was chosen in order to develop the broadest possible consensus among governmental agencies, soon-to-be regulated businesses and members of the public. The model ordinance seemed a useful device to maximize uniformity of implementation county-wide.

The task force produced a model ordinance regulating both above ground and underground facilities storing hazardous materials and hazardous wastes. The model HMSO requires both primary and secondary containment (e.g., double-walled tanks) on all new storage units and associated piping, and the capability to monitor leaks from primary to secondary containment. Existing single-wall storage units could remain in place only if monitoring systems were installed to identify any leaks. Typically, monitoring wells have been constructed near underground tanks to ensure that no undetected leaks occur. The HMSO also required Hazardous Materials Inventory Statements from each facility describing the nature and maximum quantity of all onsite hazmat, and a site plan showing the location of all storage.

The Santa Clara County Intergovernmental Council (IGC), a coordinating body of elected officials from the County Board of Supervisors, each of the fifteen cities, and several special districts, approved the model ordinance in May 1983. In the following months most cities, as well as the County (for unincorporated areas) adopted HMSOs identical to the model ordinance, or nearly so. As of early 1986 eleven separate HMSO programs cover the entire county: nine are being implemented by city fire departments; one by the County's Central Fire Protection District serving two additional cities; and one by the Santa Clara County Health Department covering the unincorporated areas plus four remaining (small) cities.

EXISTING COORDINATION MECHANISMS

The local HMSO implementers have created a number of formal and informal mechanisms to exchange information. These allow the firemen to learn from one anothers' experiences, and to work out timely and consistent responses to common issues.

The most important vehicle is a monthly meeting of the hazmat officers from each jurisdiction, organized as the Hazardous Materials Subcommittee of the Fire Chiefs' Association. Most jurisdictions in Santa Clara County send at least one representative to each session. So do hazmat units in nearby counties, and regional bodies such as the Bay Area Regional Water Quality Control Board and the Santa Clara Valley Water District. Participants discuss their programs and evaluate common approaches; one pending issue is how HMSO programs address the disposal of hazmat storage tanks that are taken out of service. Vendors of storage and monitoring technologies also appear regularly to present their products for group appraisal.

HMSO personnel also confer informally with people from the county's four publicly-owned treatment works (POTWs) who enforce pretreatment requirements for industrial sewage discharge. HMSO and POTW personnel discuss situations at the facilities being permitted and inspected by both organizations - some 620 sites county-wide.

During the winter of 1985-1986 the IGC conducted a survey of HMSO implementation county-wide. Draft questionnaires were distributed in October 1985 to each HMSO jurisdiction, and to environmental and industry activists. Comments on the draft were incorporated into a final questionnaire distributed in February 1986, with responses due by the end of March.

The questionnaire responses will provide the first detailed countywide assessment of HMSO implementation (other less detailed surveys have been conducted in the past). Policy makers will then be able to assess the scope of the program (numbers of facility permits and of tanks), the status of permitting and inspections to date, and the dollars and personnel resources implementing the programs. They will also be better able to evaluate the consistency of implementation in the various jurisdictions.

HMSO IMPLEMENTATION QUESTIONS

Policy makers throughout Santa Clara County have faced a number of generic questions in enacting and

implementing the HMSOs. Despite the useful monthly meetings of implementing personnel, many of these questions have been faced in relative isolation in each of the sixteen political jurisdictions. As policy makers throughout California and the nation prepare to implement legislatively-mandated programs, they will face many of these same questions.

What are the goals? The HMSOs are designed to regulate all above and underground hazmat storage facilities, to identify and replace leaking units, and to require double containment of all newly installed units to prevent future leaks. Most jurisdictions initially sought to have all permits and monitoring in place within two to three years, but these targets have tended to slip as the full range of start-up costs and implementation difficulties have become apparent. The difficulties in meeting these targets have generated a certain amount of unnecessary disappointment and defensiveness. To avoid such problems elsewhere, new hazmat programs should incorporate realistic goals, mindful of Santa Clara County's experience to date.

How big is the problem? When Santa Clara County communities first addressed hazardous materials storage, little accessible information existed about the numbers of above and underground storage units, either tanks or other types of containers. Fire departments and building/planning departments had some idea, but it took some effort to assemble this information into the predicate for HMSO implementation. In most jurisdictions, this recycling of information was supplemented by surveys of business license holders, referrals from other governmental agencies, and door-to-door surveys. Some inspectors even "let their fingers do the walking through the yellow pages" listing of businesses likely to store hazardous materials. Some 5,700 facilities with hazmat storage have been targeted for HMSO permitting in Santa Clara County.

California jurisdictions starting now will have a head start on this process. AB2013 (Cortese), passed in 1984, required a statewide survey of all underground storage facilities; roughly 175,000 have been registered, and lists are on file at the State Water Resources Control Board. This still leaves local agencies to verify the registry, and to track down above ground storage facilities as they implement AB2185.

How much to spend and what fees to collect? In setting up a budget for hazmat implementation, policy makers must remember that they will only get what they pay for. Start-up costs for equipment and training are likely to be

sizeable, and cannot easily be recouped unless first-year permit fees are set very high, perhaps prohibitively so. However, programs are likely to flounder without adequate preparation, both human and material. Programs cannot be expected to break even their first year or so.

Even on-going programs can be expensive for businesses and governments. The City of Palo Alto, for instance, charges up to $450 per site for a two-year permit, as part of a fee schedule that nearly covers its program costs. The tradeoff in implementing a thorough program is between two sets of grumbles: either from businesses paying higher fees or agency budgeters covering the unmet costs of the program.

Who should implement the program? Within local governments several departments might be assigned responsibility for implementation of local hazmat ordinances: fire departments; building departments; POTWs; or health departments. The choice may prove important over the long haul.

In Santa Clara County, ten of the eleven HMSO programs are implemented by fire departments. Firemen's obvious interest in above ground hazardous materials spawned the initial model ordinance task force, and led most cities to assign responsibility to their fire services.

Unfortunately, firemen have no automatic professional interest in underground storage techniques, because few underground leaks pose fire hazards. As at least one fireman has remarked in Santa Clara County, "groundwater doesn't burn." Our County's firemen have thus been led well beyond their traditional interests and expertise when implementing the underground tank aspects of HMSOs. Efforts to graft further hazmat responsibilities - such as inspecting hazardous waste generators and verifying their manifests for hazardous waste transportation and disposal - would lead them even further afield. As hazmat responsibilities are expanded by legislative mandates, a fire-based program may eventually reach a dead end; after all, how broad are the career opportunities for firemen whose primary expertise lies in evaluating underground storage and monitoring devices? Some fire departments have begun to hire people with skills especially appropriate to hazmat regulation. The City of Santa Clara now has three chemists on its fire staff, and Sunnyvale recently transfered one chemical waste inspector from its POTW to the fire department hazmat unit. Future career paths for these personnel are unclear, however.

An alternative lies in health departments in counties and a few cities. Here, the inspection and

monitoring skills are integral to other responsibilities, as is the professional focus on long-term health impacts. But concerns for above-ground storage may be somewhat less immediate than for fire services. Santa Clara County has assigned its HMSO program, covering unincorporated areas and four small cities, to a Hazardous Materials Unit within the County Health Department. This unit will also assume the new duties under AB2185 and soon will begin to inspect hazardous waste generators under a memorandum of understanding (MOU) with the State Department of Health Services.

Sanitary engineers at POTWs are also professionally attuned to at least some hazmat functions, and are already involved in inspection and monitoring under their pretreatment programs. Here, the limitation comes as responsibilities grow beyond "wet" (sewered) wastes to "dry" (non-sewered) wastes.

If hazmat responsibilities are assigned to non-fire units, an interdepartmental coordinating function automatically becomes necessary, since firemen still need emergency response information. In any event, AB2185 requires some sort of centralized county-level information center. This will require either duplicate records or a reliable data transfer system.

How many hazmat programs? Coordination issues become more acute as hazmat responsibilities proliferate. Policy makers - whether voluntarily or under mandate from a higher authority - may divide hazmat responsibilities among a number of departments. Extra care must then be taken to ensure that some tasks aren't being performed twice while others lie forgotten.

Care should also be taken to assure consistency among programs operated by each jurisdiction, and also among similar programs operated by contiguous jurisdictions. Nothing is more frustrating than being required to cope with inconsistent or even conflicting demands from different agencies. Consistency also increases the fairness of the overall effort, and reduces temptations to play off jurisdictions against each other.

In Santa Clara County, this means that local officials must develop effective coordination among four closely-related hazmat programs during 1986:

- HMSO (11 local programs)
- POTW pretreatment (4 programs)
- AB2185
- Hazardous waste generator inspections under MOU

Program planners are now sketching options for coordinating (and perhaps integrating) elements of these four programs.

An ideal result would be one-stop regulation of all hazardous materials and hazardous wastes, at least from the regulated business person's perspective. One immediate goal is to ensure that one permit filing will satisfy the requirements of both the HMSO and AB2185 by amending the HMSOs to require information required by AB2185. Another target is consolidated, or at least coordinated, inspections under the various programs. A unified permit fee structure would also reduce businesses' steps to full compliance.

CONCLUSIONS

This paper has described briefly the Santa Clara County experience with HMSO implementation. We expect that other local governments will experience many of the same frustrations and uncertainties we have, and so will benefit from our discoveries.

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USE OF BUFFER ZONES IN THE CONTROL OF HAZARDOUS MATERIALS: A CASE STUDY

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INTRODUCTION

This paper presents a case study evaluating the use of a buffer zone to reduce the risk of public exposure to potential hazardous materials releases. A buffer zone is an imposed space of land designed to separate an area of hazardous materials activity from sensitive human populations. An overlay district, familiar to most city planners, is a more refined version of a buffer zone. In this report an overlay district is considered a buffer zone. The objectives of this study were: (1) to obtain an unbiased assessment of the Fremont hazardous materials management plan, and (2) to determine if the use of a buffer zone would contribute an additional margin of safety for the protection of human health.

CASE STUDY BACKGROUND

The "Silicon Valley" in the northern California County of Santa Clara has been an area of high technology based industrial activity over the past 20 years. The continued growth of high technology industries has created a continually expanding need for additional office and manufacturing space in the Bay Area. Recently, the City of Fremont, on the northeastern border of Santa Clara County, has been a major site of similar high tech industrial development. Concern in Fremont about the impact of hazardous materials on human health has increased with the increased industrial activity.

Evidence of contamination of the local environment from industries utilizing hazardous materials in other cities has created citizen concern for the public health in the City of Fremont. Many of those incidents occurred in spite of the existence of governmental regulations designed to reduce the risk of public exposure.

Public concern for the quality of health in Fremont has prompted the City to reassess hazardous materials management programs currently in effect, and to determine if additional measures can be taken to decrease the risk to public health from accidental hazardous materials releases.

METHODS

The hazardous materials management study was divided into the following four phases: (1) assessment of the existing legislation regarding hazardous materials, (2) identification of the geographical profile of industrial and residential areas in Fremont, (3) assessment of the Fremont local hazardous materials ordinance, and (4) evaluation of the effectiveness of a buffer zone as a possible means to mitigate residential exposure to hazardous materials releases.

EVALUATION AND DISCUSSION

Current Regulations

The general definition of a hazardous material and/or waste, as used herein, is any substance or mixture of substances which presents a real or potential hazard to human health or the environment. A more complete definition appears in the California Administrative Code (CAC), Title 22, Division 4, Section 66084.

Several federal, state, and local agencies have been given the authority through a myriad of legislation to regulate hazardous materials. In California, state legislation both augments and/or supplements the federal legislation. In fact, many of California's hazardous materials regulations have served as a model for other states, and even federal hazardous materials regulations, such as the Hazardous and Solid Wastes Amendments of 1984 (EPA, 1985). Therefore, one must be aware that many California regulations which govern hazardous materials activities are in effect.

Table 1 is a summary of the federal, state, and local legislation which is applicable to the regulation of hazardous materials in the City of Fremont. These numerous regulations have overlapping requirements which govern the of management hazardous materials and wastes in air, water, and land, as well as during transportation, and industrial activity. A more comprehensive review of the regulations may be found in the various federal and state codes listed in Table 1.

Fremont Geographic Profile

Every community has a unique density and distribution of industrial and residential areas. The City of Fremont is concerned that its industrial growth could present an increased risk to public health from a potential hazardous materials incident. Hazardous materials management concerns for the City of Fremont stem from the following: (1) rapid industrial growth, (2) location of residential areas near the industrial zoned lands, (3) transportation of hazardous materials within the city limits, and (4) predominance of specific types of industrial activity.

Table 2 summarizes the pertinent size of the seven industrial areas and gives an estimate of the closest residential areas of Fremont. The Warm Springs District contains a residential population which is located nearest to Fremonts largest industrial area in Fremont. This sensitive area would likely be a candidate for consideration of the use of a buffer zone.

The residents located along the major truck and train transport routes represent a human population potentially sensitive to releases during hazardous materials transportation. These transportation routes essentially form a network of roads and railway lines which in effect cover the entire city of Fremont. A hazardous materials incident occurring during transport could essentially effect any part of the City. However, the City cannot control the transportation of hazardous materials on State highways; therefore, little can be done locally to protect residents along transportation routes.

One type of industry, the electronics industry, has been predicted to be predominant within the industrial areas of Fremont. The other industries

will most likely be machine and plating shops, and to a lesser extent, chemical and allied products manufacturing. Currently computer and electronics industries comprise nine out of the 12 major employers within the City of Fremont.

Toxic and or combustible liquids and gases have been identified as materials which have the greatest potential to affect public health. Hazardous gases can contaminate the atmosphere and hazardous liquids can contaminate soil and/or groundwater. In addition, some hazardous materials have explosive and/or flammable properties. In a study prepared by the California Department of Industrial Relations (DIR), approximately 280 chemicals were identified which were used by the semiconductor industry in Santa Clara County (DIR, 1981). The 43 hazardous materials most used by the electronics industries in 1979 were solvents and several toxic gases (Table 3). We assume these materials will be used by the industries moving into the City of Fremont.

Assessment of the Local Ordinance

The City has adopted its own hazardous materials management regulations (Local Ordinance 1632). The regulations were modeled after the Santa Clara County ordinances, as well as several other local underground tank ordinances. The local hazardous materials ordinance was accepted by the State Water Resources Control Board (SWRCB, August, 1985). The ordinance meets the State requirements set aside in the California Administrative Code (CAC) Title 23 Subchapter 16, for hazardous materials storage regulations.

Ordinance 1632 has a total of 14 articles, six of which dictate specific actions required for storage and use of hazardous materials. Very few inadequacies were identified in the ordinance. However, an ordinance is only as good as its implementation. Our evaluation indicated that the City was unable to implement the ordinance due to inadequate staffing. Our recommendations included the following: staffing requirements to adequately implement the ordinance, and a plan for the funding of the required staff.

Effectiveness of a Buffer Zone

No set of regulations can totally prevent an accidental release of a hazardous material. Concerned citizens, highly sensitive to the presence of hazardous materials in the local environment, have proposed the addition of buffer zones to protect public health in the event of a hazardous materials release. Theoretically, a buffer zone should function to geographically isolate residential areas from industrial areas which have hazardous materials activities. This buffer zone would function as a mechanism for reducing exposure to sensitive populations by diluting the an accidentally released volume of hazardous materials and by allowing time for emergency response actions to occur before exposure occurs.

Currently, no Federal regulations exist regarding buffer zones for hazardous materials. The California Health and Safety Code, Division 20, Chapter 6.5, Section 25117.4, describes a "Border zone property" of 2,000 feet to be placed around any significant hazardous waste disposal sites. This 2000 foot distance was chosen somewhat arbitrarily, and is subject to appeal in individual cases. California Senate Bill 532 (Stiern) was passed in the Senate on June 3, 1985. This bill directs the DHS to require the owners of hazardous waste facilities to provide at least a 2,000 foot buffer zone. If the owner does not own all of the property located in the buffer zone, he must purchase the property at fair market value from the adjacent

land owners. SB 532 is now under consideration in the Assembly Environmental Safety and Toxic Materials Committee.

Durham, North Carolina, is a city which has enacted a buffer zone ordinance exclusively dealing with hazardous wastes. In this case, only hazardous waste facilities were regulated because a hazardous waste recycling facility was to attempting to locate in Durham. Citizen concerns for public health and safety generated the buffer zone ordinance.

Essentially, the Durham ordinance requires all industries which handle hazardous waste to have a 1,250 foot buffer zone between the area of hazardous waste activity and any area zoned residential. The 1,250 foot buffer distance was arrived at through arbitration between the citizens, industry, and the city. The buffer zone distance was not based upon any specific scientific or engineering principles. However, passage of the buffer zone ordinance appeased the local citizens' concern for public health. It should be noted that the Durham buffer zone does not affect facilities which use hazardous materials.

To judge the effectiveness of a buffer zone for Fremont, a hazardous materials incident was simulated. We used a worst-case scenario to determine the potential areas of impact for a toxic gas. The atmospheric concentrations for a release of chlorine were developed using an air dispersion model in an Environmental Impact Report (EIR) prepared for the City (Fleur, 1983).

In our scenario a tanker truck hauling a load of chlorine is involved in an accident on highway I680 near Mission Boulevard at approximately 10:00 AM. A transportation incident, rather than an industrial incident simulation, was chosen as requested by the City. However, the release might have happened in the many other areas of the City. Assuming that 150 pounds of materials is released in 2 mile per hour stable wind conditions the area exposed to significant risk would extend up to 1000 yards downwind from the leak site. The number of people exposed to this released chlorine would depend on the number of people present in the exposed area. In a hazardous materials incident of this magnitude, a buffer zone surrounding the release site would not have been effective.

We recommended that wind and weather data be available to emergency response teams at any time. In the event of an actual release, immediate meterological conditions would be vital information.

The actual extent of hazard exerted by an airborne hazardous material release would depend upon the toxicity of the specific material(s), the amount of material released, the prevailing meterological conditions, the size of the exposed population, and the emergency preparedness of the affected community. In some hazardous materials releases, such as the transportation scenario, a buffer zone would not be an effective measure for reducing the potential for public health exposure. Conversely, in some instances such as a fire and/or an explosion, a buffer zone could be beneficial.

Each hazardous materials incident has specific characteristics, as discussed above. For example, if all the specific conditions of release prohibited the hazardous material from traveling very far from the source of release, then a buffer zone of some arbitrary size would function to separate a hazardous materials release from a local population.

The local geography of the southern industrial area in Fremont offers a natural buffer zone for the residents of the Warm Springs District. Warm Springs Boulevard forms a buffer zone between residents and industry in that district. The Boulevard is approximately 100 feet wide and separates the industrial buildings from the residential areas. In addition, much of the industrial development is planned for the west side of Highway 880. The highway could act as a buffer zone between the residential areas east of Warm Springs Boulevard and the new industrial areas. This type of buffer zone may be effective as protection from hazardous materials releases resulting in fire and/or explosions. In some catastrophic events, however, a natural buffer zone of this type would not offer adequate protection for the residents. There is no real buffer zone protection available for such an event as occurred in Bhopal, India where a toxic gas plume migrated approximately 25 square miles through the city.

RECOMMENDATIONS

In Fremont, a buffer zone placed between existing industrial and residential areas is not feasible. To completely separate the residential areas from the industrial areas, either the residents or the industries would have to move. It may not be reasonable to consider either of these two options. However, for new industrial and/or residential zoned lands, a buffer zone should be considered to protect against fire and minor hazardous materials incidents as well as addressing private citizens concerns.

Some components of a hazardous materials release can and are regulated by means other than a buffer zone. The following items can be regulated: the amount of material released based upon storage limitations, the emergency response preparedness of the affected facility, and the implementation of an approved hazardous materials ordinance. These controls cannot be accomplished through the use of a buffer zone, but rather are accomplished through building codes, storage regulations, etc. Theoretically, if the hazardous materials regulations are rigorously enforced in a city then a buffer zone measure may not be necessary.

It is apparent that the use of buffer zones for the City of Fremont may not contribute an additional margin of safety for the protection of human health in all hazardous materials releases. A hazardous materials incident could occur in the City with or with out the presence of a buffer zone. A buffer zone ordinance could be used to address the concerns of Fremont citizens. However, other options such as limiting the bulk volume storage of selected hazardous materials and rigorously implementing the existing hazardous materials management plan may provide a more viable solution to the public health concerns regarding hazardous materials usage in the City of Fremont.

The final resolutions concerning buffer zones for the City of Fremont have not yet gone to public hearing. The next phase of the Fremont study will include the following: (1) the buffer zone study will be used by the City as an Environmental Impact Report (EIR), (2) the results of the buffer zone study will go to public hearing, (3) public comments will be received and incorporated into the report, and (4) public workshops on the results of this study will be organized for Fremont citizens.

REFERENCES

California Department of Industrial Relations, Task Force on the Electronics Industry, 1981. Semiconductor Industry Study.

Fleur, Larry, 1983. Earth Metrics, 1983. Larry Fleur, Inc.

California State Water Resources Control Board, August 12, 1985. Underground Tank Program Administering Agency List.

EPA, 1985. Federal Register, October 29, 1985, Vol 10(209):44635.

Table 1. Federal, State, and Local Hazardous Materials Legislation

	Responsible Agency	Regulations	Reference
Federal Regulations	DOT[1]	Hazardous materials transportation	CFR[2] 49
	EPA[3]	Underground storage tank registration	CFR 40
	EPA	Hazardous materials release reporting	CFR 40
State Regulations	DHS[4]	Hazardous waste regulations	CAC[5] 22,
	DMV[6]	Hazardous materials transportation	CAC 13
	CHP[7]	Hazardous materials transportation	CAC 13
	OES[8]	Hazardous materials incident response	CAC 19
	ARB[9]	Air pollution control regulations	HSC[10] Division 26
	SWRCB[11]	Water pollution control laws	CAC 23
Local Regulations	City of Fremont	Hazardous materials management	Local Ordinance 1632

1. DOT - Department of Transportation
2. CFR - Code of Federal Regulations
3. EPA - Environmental Protection Agency
4. DHS - Department of Health Services
5. CAC - California Administrative Code
6. DMV - Department of Motor Vehicles
7. CHP - California Highway Patrol
8. OES - Office of Emergency Services
9. ARB - Air Resources Board
10. HSC - Health and Safety Code
11. SWRCB - State Water Resources Control Board

Table 2. Summary of Industrial and Nearby Residential Area Development for Fremont

Industrial Area	Approximate Total Acreage	1980 Local Population
1. Southern	5,740[a]	7,920[b]
2. Northern Plains	390[c]	6,190[d]
3. Centralmont	60[c]	13,277[e]
4. Mission Boulevard-King Avenue	60[c]	7,409[f]
5. Shinn Street	70[c]	7,546[g]
6. Niles Canyon - Amchem	<2[h]	7,409[f]
7. Lake Elizabeth Plaza	20[c]	6,820[i]

a. Fremont Community Development Department, Fremont an Economic Profile, June, 1985

b. Fremont Planning Department, Warm Springs District Census Tract, 1980.

c. Fremont Chamber of Commerce Industrial Area Map, April, 1985.

d. Fremont Planning Department, Ardenwood Forest Development Plan, November, 1981.

e. Fremont Planning Department, Centerville District selected Census Tracts, 1980.

f. Fremont Planning Department, Niles District Census Tract, 1980.

g. Fremont Planning Department, Irvington District selected Census tracts, 1980.

h. Fremont Planning Department Map, September, 1984.

i. Fremont Planning Department, Mission-San Jose selected Census Tracts, 1980.

Table 3. Material Usage Table - 1979 Semiconductor Industry Study 1981[a]. Division of Industrial Relations, Department of Occupational Safety and Health

Solvents	Gallons[b]
Isopropanol (2-Propanol)	>131,940
n-Butyl Acetate	> 91,970
Freons	> 85,280
Xylene	> 74,210
Acetone	> 64,250
Methanol	> 51,810
Petroleum Distillates	> 25,390
Trichloroethylene	> 22,740
1,1,1-Trichlorethane (Methyl Chloroform)	> 16,310
Methylene Chloride (Dichloromethane)	3,810
Tetrachloroethylene (Perchloroethylene)	1,320
Ethylene Glycol	800
Methyl Ethyl Ketone (2-Butanone)	> 730
Hexamethyldisilazane (10%) (HMDS)	> 550
Ethanol	> 130
Toluene	60
Chlorobenzene	10

Acids	Pounds		Gallons[b]
Sulfuric	156,600	and	>396,400
Hydrofluoric Acid	34,200	and	>207,790
Hydrochloric Acid	13,300	and	>336,600
Phosphoric Acid	16,800	and	> 32,350
Ammonium Fluoride	5,500	and	> 89,780
Acetic Acid	3,300	and	>340,350
Nitric Acid	4,500	and	>135,260
Boric Acid	800	and	> 10
Citric Acid	8	and	100
Buffered Oxide Etch (Hydrofluoric Acid & Ammonium Fluoride)			23,500
Fluoboric Acid			80

Table 3. Material Usage Table - 1979 Semiconductor Industry Study (cont'd)

Caustics	Pounds
Sodium Hydroxide	540,100
Ammonia	86,700
Potassium Hydroxide	35,670
Ammonium Hydroxide	8,130

Gases and Liquids - Summary

Gas[c]	
Hydrogen Chloride	834,807
Silane	253,537
Phosphine	211,370
Ammonia	158,381
Arsine	64,068
Diborane	26,490
Boron Trifluoride	1,497
Krypton 85	10

Liquid[d]	
Silicon Tetrachloride	83,910
Trichlorosilane	50,594
Boron Tribromide	43,377

a. Reference: California Department of Ind. Relations, Division of Occupational Safety and Health, 1981.

b. Figures rounded to nearest 10 gallons. The greater than sign indicates an undisclosed amount from one or more companies. Both pounds and gallons were reported. These figures were not combined because final concentrations were not specified.

c. Reported in cubic feet - unspecified concentrations.

d. Liquids usage quantities were reported incorrectly as cubic feet versus gallons or pounds.

TRANSPORTATION OF HAZARDOUS WASTES RISK ASSESSMENT FOR LOCAL ACCESS ROUTES IN THE VICINTIY OF EXISTING AND PLANNED DISPOSAL FACILITIES

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1.0 INTRODUCTION

In February 1985, SCAG produced the Transportation Component of Phase II of the Southern California Hazardous Waste Management Project. Phase II was authorized in November 1983 through a "Memorandum of Understanding" signed by SCAG, SANDAG, and Santa Barbara County-Cities Area Planning Council. The project included tasks to develop a regional siting and planning strategy, and "assess transportation routing and risk issues".

The purpose of the "Transportation of Hazardous Waste. Southern California Hazardous Waste Management Project" February 1985. study (1) was:

To assess the risks involved in the transportation of hazardous wastes by both road and rail in the 8-county study region (including Santa Barbara and San Diego), and to recommend methods for reducing those risks;

To develop a series of safe transportation routes and management procedures, that will carry hazardous waste from its center of generation to its point of disposal in the 8-county study region.

This paper focuses on highlighting the technical work from the study that addressed the following questions:

What are the characteristics that make one route preferable to another from the perspective of improving public safety when transporting hazardous wastes? What routes have the smallest probability of an accident and least adverse impacts if hazardous wastes are released? The study developed a regional accident data base and a methodology for risk assessment (which also can be used by other agencies in the region).

The paper explains the study methodology and findings for assessing risks on local access routes to possible disposal facilities. From the perspective of improving public safety when transporting hazardous wastes, the study identified such risk factors as :

Characteristics of studied disposal facilities
Accident data
Hazardous waste truck volumes
Comparison to statewide average rates
Comparison of accident rates on routes in the vicinity of planned facilities to those of the existing landfills
Determination of route "risk indices"
Populations potentially at risk

In addition, the study also analyzed hazardous waste manifest and hauler registration procedures, and developed recommendations to improve highway safety through better communication from generator to transporter, and to increase education and training levels of all involved in the proper off-site disposal of hazardous wastes. These findings are not presented in this paper (please see the above full study report for details).

2.0 COLLECTION AND ANALYSIS OF ACCIDENT DATA ON REGIONAL HIGHWAYS

Task 1 of the Work Program calls for the determination of highway risk factors involved in the transportation of hazardous wastes. The first and most important step is the analysis of accident data and identification of routes or roadway segments exhibiting high accident rates. Review of traffic safety and operations literature and extensive conversations with Caltrans, CHP, and other local traffic agencies revealed that the best indicator of the safety history of a particular stretch of roadway is the "accident rate"; i.e., the number of accidents recorded per million vehicle miles (acc/MVM).

2.1 THE ALL-VEHICLE ACCIDENT RATE

The rate is based on current daily traffic volumes, the number of accidents recorded in police records, facility design standards, and the length of the segment. In the case of state highways, rates are based on 4-year histories of CHP recorded data (Jan. 1980 to Dec. 1983).

The accident rates used in this study apply to all vehicle types involved in accidents, from trucks to motorcycles, and is an index of the relative safety history of a <u>stretch of roadway</u>. Accident rates in no way reflect the safety record of <u>one single type of vehicle.</u>

The overall accident rate is an important characteristic of a given segment of highway. Traffic agencies recognize that there are characteristics that can make one roadway less safe than another (geometrics, signaling, congestion, etc.). These agencies including Caltrans and the California Highway Patrol (CHP) use overall accident rates to identify trouble spots and to rank safety projects in the State Transportation Improvement Program (STIP). The safety record of the hazardous waste haulers may well be good, but hazardous waste trucks are at greater risk if they travel on roadways that have higher accident rates. Avoidance, where possible, of "high risk" roadways can clearly benefit hazardous waste truckers.

The "all-vehicle accident rate" is used to calculate Caltrans' "Safety Index". This safety index is the key to Caltrans' methodology for ranking HB-1 (Safety) highway projects greater than 0.5 miles in length. An "average accident reduction" is then calculated for proposed improvements, such as new signals, left-turn channelization, curve corrections, and shoulder widening. The priority number of such a project determines the year of allocation of funds, within the 5-year STIP cycle.

The U.S.D.O.T./Federal Highway Administration has published "Guidelines for Applying Criteria to Designate Routes for Transporting Hazardous Materials". Here a methodology to calculate the probability of a hazardous material accident has been developed. These guidelines state:

"To calculate this probability the analyst derives <u>the accident rate for</u>

all vehicles and then factors that rate to reflect the much smaller share of hazardous material vehicles in the traffic stream ......" (2). Even if the rate is further factored to reflect hazardous waste vehicles in the traffic stream, the "all vehicle accident rate" is considered crucial to the overall federal methodology. Furthermore, this FHWA methodology has been adopted in SB 2030 (Hart) and AB 1861 (Campbell).

2.2 GENERAL FINDINGS

Our analysis showed that only a relatively small portion of the regional freeway system was identified as having accident rates above the statewide average or SWA (some segments along I-110, I-5, Rt.101, Rt.55). Clearly, almost all of the freeway system exhibits rates that are equal to or below the SWA. These results confirm previous SCAG analyses that maintain that the freeway system is by far the safest of all the various highway facility types.

3.0 RISK ASSESSMENT FOR LOCAL ACCESS ROUTES IN THE VICINITY OF THE PLANNED BKK TREATMENT FACILITY AT WILMINGTON

Once accident rates were calculated, for the major state highways in the 8-county study region and an assessment of which segments were above the statewide average, it was possible to see the relative safety of major access routes to existing and proposed hazardous waste activities. These activities include existing landfills, planned treatment facilities, and Superfund Clean-up sites.

Hazardous waste trucks - after leaving the freeway system - will use local streets and roads to access local disposal sites. Thus more detailed accident data is needed for these streets and roads, in order to analyze the relative safety of the complete assess route.

When the L.A. City Council previously approved the EIR and a number of access routes for the planned BKK Wilmington Treatment Facility (APTEC 1), Staff felt that this proposal was a logical place to begin an early action program to gather safety data on local access routes. and to look at the rail alternatives in the vicinity - see report "Potential for Hazardous Waste Transportation by Rail" (1). The Wilmington analysis was intended to be a prototype for the analyses of other specific hazardous waste disposal sites.

3.1 CHARACTERISTICS OF THE PLANNED BKK WILMINGTON TREATMENT FACILITY

The previously proposed BKK Wilmington Treatment Facility project site is located at East "I" Street between the Terminal Island Freeway and the L.A./Long Beach city line (see Figure 1). The facility would treat liquid hazardous wastes and BKK hopes that 70% of the volumes previously disposed at the BKK West Covina Landfill will be treated at the BKK Wilmington Treatment Facility if built. The project would generate 87 daily inbound tankers each carrying 5000 gallons of liquid hazardous wastes (3). Trucks can access the site using many alternative routes -- from Los Angeles on the west and from Long Beach on the east.

FIGURE 1

ROADWAY SEGMENTS IN THE VICINITY OF PLANNED TREATMENT CENTER WHERE ACCIDENT DATA ANALYZED

(dotted line)	STATE HIGHWAYS
(dashed line)	LOCAL STREETS AND ROADS
*	TREATMENT SITE LOCATION

3.2 COLLECTION OF ACCIDENT DATA

Accident data were collected from 3 sources: Caltrans, City of Los Angeles Department Of Transportation, and the City of Long Beach Traffic Department. The standard comparative accident index was utilized for the analysis -- namely: accidents per million vehicle miles (MVM). These rates were available for Caltrans and LA City routes, but had to be calculated for Long Beach streets using raw data. The following is the standard formula that was used to calculate the rates for Long Beach streets:

$$\text{Acc/MVM} = \frac{\text{Total number accidents (recorded in police records)}}{\text{ADT X 365 X Route Segment Length/1,000,000}}$$

3.3 COMPARISON TO STATEWIDE AVERAGE RATES

Statewide average (SWA) rates for the different roadway facility types were based on Caltrans' 1981 and 1982 Reports "Accident Data on California State Highways".

- o Freeways in Urban Areas — 0.8 - 1.5 Acc/MVM.
- o Undivided Conventional Highway (4 plus lanes) in Urban Areas (e.g. P.C.H.) -- 5.5 - 6.0 Acc/MVM.
- o Given the above rates it was therefore assumed that a 2-lane conventional highway in an urban area would probably have a SWA rate of at least -- 7.0 - 8.0 Acc/MVM.

3.3.1 STATE HIGHWAYS

Historically freeways have by far the lowest rates of all highway facility types. Five state highways were examined : I-405, I-110, I-710, 47, and Pacific Coast Highway (PCH). Although most of the rates were close to the freeway SWA, there were variations within the range (0.4 - 5.3 acc/MVM), with the the Interstates having the lowest rates and PCH the highest (see segment I-710 to Rt.47). Caltrans rates reflect data collected over the 4-year period from 1980 to 1983.

3.3.2 LOS ANGELES CITY STREETS

Six streets in the City of Los Angeles were analyzed: Anaheim, Lomita, PCH, Alameda, Avalon and Wilmington for 1980, 81, and 82. Most of the streets were not problematic but a few segments were above the SWA.

Alameda -- Henry Ford Avenue to Anaheim St. (10.0 - 15.0 acc/MVM).
Avalon -- Anaheim St. to 'B' St (8.0 - 11.0 acc/MVM).
Wilmington -- Denni to 'B' St.

The intersections of Anaheim/Henry Ford Avenue and Anaheim/Alameda appeared to have a high number of accidents. In addition, data were received from LAPD records (1981), which rank all City intersections by number of accidents recorded. Out of 1035 intersections, the Anaheim/Wilmington was 33rd highest (worst) and Avalon/PCH 65th highest.

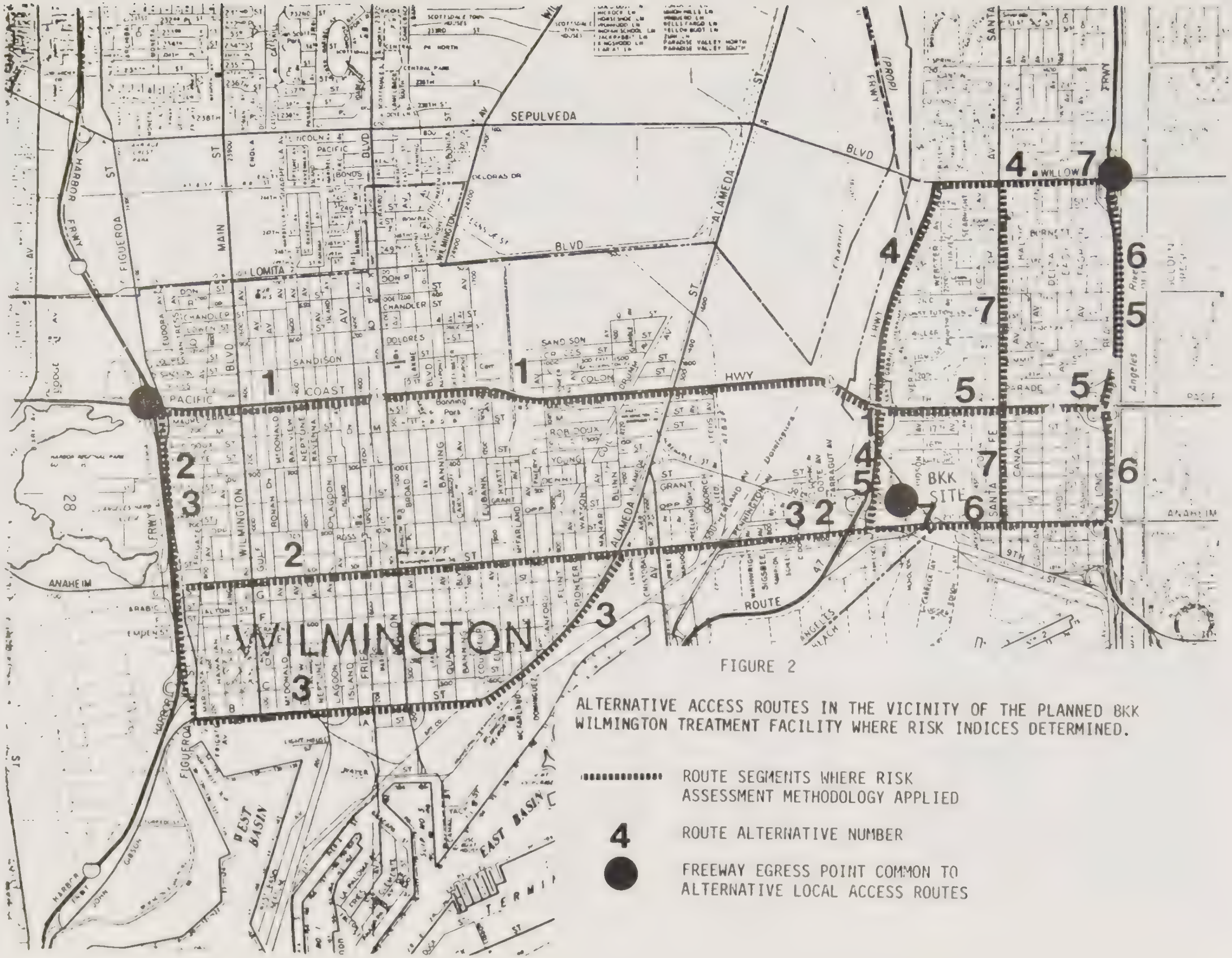


FIGURE 2

ALTERNATIVE ACCESS ROUTES IN THE VICINITY OF THE PLANNED BKK WILMINGTON TREATMENT FACILITY WHERE RISK INDICES DETERMINED.

3.3.3 LONG BEACH STREETS

Six streets in the City of Long Beach were analyzed: Anaheim, PCH, Willow, Santa Fe Avenue, and Rt.7 for the same years. Raw data were taken from local police records available through the "SWITRS" system. Only on Santa Fe Avenue between Willow and 9th were rates above average (8.0 - 12.0 acc/MVM). All other streets had rates that were average or below average.

3.4 CALTRANS' MAJOR TRAFFIC INCIDENT MANAGEMENT PROGRAM DATA

Data for 1982 show that Caltrans responded to 19 "major" incidents (2 or more lanes being closed for 2 or more hours) which occurred in the vicinity of the I-405/Rt. 7 interchange. This represented the highest concentration of incidents in the region. However, in 1981 there were only 4 incidents at this location; in 1980, 5 incidents; and in 1979, 4 incidents.

3.5 TRUCK INVOLVEMENT

Caltrans data showed demonstratively that, of all accidents recorded, I-710 (between I-405 and Delamo) and Rt. 47 (between PCH and Anaheim) respectively had the highest percentages of "large" truck involved. This finding is consistent with fact that on I-710 (Willow to I-405) trucks constituted 21% of all vehicles; and 15% on Rt. 47 (Ocean to Anaheim) (4).

3.6 COMPARISON OF ACCIDENT RATES ON ROUTES IN THE VICINITY OF THE PLANNED WILMINGTON FACILITY TO THOSE OF THE EXISTING LANDFILL ON AZUSA AVENUE

The next stage of the analysis was to look at the accident history along Azusa Aveune which provided the only local street access to the now closed BKK West Covina Landfill. Of the 110 or so trucks per day that entered the landfill (prior to closure), about 70 of these were expected to be diverted to the planned BKK Wilmington Treatment Facility. Thus, the relationship of high concentrations of hazardous waste truck traffic to the accident rate on Azusa Avenue can be analyzed.

Data collected from the City of West Covina and L.A. County Road Department for the 7 segments of Azusa Avenue between I-10 and Rt.60. showed that accident rates for both I-10 and Rt. 60 accessing the landfill were not above the SWA for freeways. Data on Azusa Avenue for 3 years (1980, 1981, and 1982) revealed that only one small segment of 0.27 miles had a rate that is considered problematic (from Amar Road to the landfill entrance). It should be noted that of all the accidents that occurred here, the percentage of trucks involved or the relationship to incidence of "spills" is not known.

In conclusion, this analysis showed that accident rates on and around Azusa Avenue were generally below the SWA, despite the high concentration of hazardous waste truck traffic.

3.7 DETERMINATION OF ROUTE "RISK INDICES"

Task 1 of the Transportation Component of the Southern California Hazardous Waste Management Project called for the identification of highway risk factors from the perspective of improving public safety when transporting

hazardous wastes.

Accident and truckload volume data were previously analyzed for routes in the vicinity of "urban/close-in" disposal site locations (Wilmington and West Covina) and for routes accessing the Kettleman Hills and Casmalia disposal sites. In addition, staff analyzed the transportation characteristics of a "remote" area location -- using the IT Corporation site in Westmorland in Imperial Valley (see later).

As the BKK Wilmington site was previously the only major treatment facility planned in Southern California, and given the closure of BKK West Covina to liquid hazardous wastes, the determination of alternative route risk factors in this location appeared to be logical. In addition to the previous factors analyzed for each route, a methodology was developed to estimate of the number of people which could be potentially impacted by a worst-case incident from trucks enroute to existing and future disposal locations.

The study of the previously proposed BKK Wilmington Treatment Facility site presented a clear opportunity to evaluate the risk characteristics that make one access route preferable to another, namely, the comparison of 7 possible access routes -- all of which can access the site from a common freeway egress point. For purposes of more accurate comparisons common egress points were defined. It is assumed that all trucks accessing the BKK Wilmington Treatment Facility site from the west will pass through the I-110/PCH junction, and those from the east (via Long Beach), through the I-710/Willow Street junction (see Figure 2).

Three alternative routes were identified from the west - from Jct. I-110/PCH to the BKK Wilmington Treatment Facility site - and 4 from Long Beach to the site (see Figure 2). Because the resultant risk indices are a function of the length of the access route, a comparison of the western and eastern access route risk indices is less meaningful.

3.7.1. POPULATION POTENTIALLY IMPACTED

In addition to analyzing accident rates, "population potentially at risk" was identified for individual roadway segments, and totalled for the total local access route, leading to the site. Following the concept in the Federal Guidelines (2), population adjacent to haulage routes combined with their accident probability can give an indication to "population at risk" in the (unlikely) event of a worst case incident.

The methodology involved estimating residential population within a 1/2 mile swath on each side of the alternative access routes. The 1/2 mile distance criterion was based on data contained in DOT's Hazardous Materials Emergency Response Guidebook (1980), the Federal Guidelines, and the Portland, Oregon Study (5). Population was based on the 1980 Census and analyzed at the census tract level. An estimation of the percentage of each census tract covered by the swath was made. Where possible, it was further adjusted when land uses were known. The various segments within each access route were defined by those segments on which accident rates had previously been calculated.

3.7.2 DEFINITION OF RISK INDEX

Populations potentially at risk were combined with the accident rates for various segments and a risk factor or index was calculated for each

segment. Segment indices were then totalled for each alternative access route for comparison purposes. The simple risk index formula can be expressed as follows:-

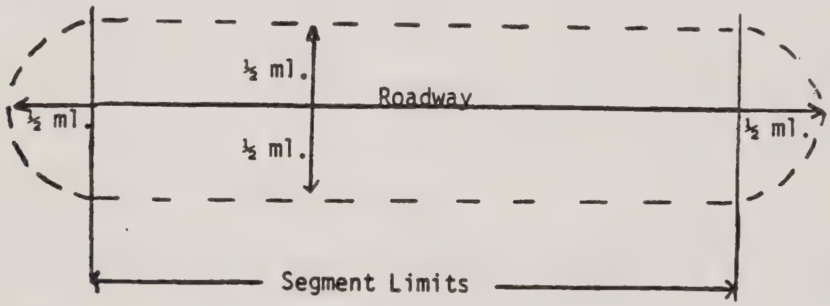
$$\text{Risk Index} = \sum_{1=1}^{n} AR_i * POP_i$$

where AR_i = accident rate for roadway segment i;

POP_i = residential population within 1/2 mile along roadway segment i;

n = number of segments in the route.

Each segment created a "sausage-shaped" swath as population in the semi-circular "ends" were still at risk if an incident was to occur near the ends of a particular segment (see diagram below). Even though the populations in the semi-circular swath ends overlapped between segments, double-counting was considered acceptable because each segment has an independent risk index. These independent indices are then accumulated for each alternative access route. In the case of the Wilmington analysis the various alternative routes have approximately the same number of segments, and thus the extent of double-counting is consistent between them. In cases where routes had significantly fewer segments, double-counting would be less, and thus populations at risk for that route would be less. Under these circumstances the system of double-counting would be considered unacceptable.



3.7.3 SUMMARY OF FINDINGS

The following list is a summary of the overall risk index for each of the 7 access alternatives (see Figure 2):

A) From the west (Jct. I-110/PCH).

Alternative	1. PCH, Rt. 47	139,119
	2. I-110, Anaheim	132,864
	3. I-110, B St, Alameda, Anaheim	35,764

B) From the east (Jct. I-710/Willow St.)

	4. Willow, Rt. 47	112,268
	5. I-710, PCH, Rt.47	87,154

6.	I-710, Anaheim	43,056
7.	Willow, Santa Fe, Anaheim	207,153

From the above, it is clear that Access Alternative 3 presents the lowest risk index for the western access routes. Alternatives 2 and 3 exhibit indices about 4 times as great. Again, the methodology shows that Alternative 6 is clearly preferred over the other eastern access routes. The identification of such clear preferences should render any discrepancies caused by double-counting insignificant. It should also be noted that Alternative 3 is the same route that L.A. City Council adopted for waste haulage access from the I-110 to the BKK Wilmington Treatment Facility (if ever built).

These results simply mean that based on roadway accident history, and surrounding number of residents, the risk - in terms of probability and magnitude of exposure to hazardous waste materials - appears to be significantly reduced with Alternatives 3 and 6.

It should also be stressed that hazardous waste haulage trucks are subject to annual inspection by the CHP, and responsible companies have maintenance and training programs. It is thus likely that the specific accident rates for vacuum, tank, and dump trucks are lower than the average for all types of roadway vehicles. However, despite the good safety record of hazardous waste haulers, hazardous waste trucks are still at greater risk if they travel on roadways that have higher overall accident rates.

4.0 RISK ASSESSMENT FOR ROUTES ACCESSING THE IT CORPORATION WESTMORLAND SITE

The next stage of the analysis was to look at the transportation characteristics of a "remote" area location -- using the IT Corporation site in Westmorland in Imperial Valley as a case study. Because the Westmorland site is the only other major receiver of Group 1 Wastes (see definition in study report) in Southern California and given the closure of BKK West Covina to liquid hazardous wastes, this facility appeared to be the next logical case study.

This site presented a clear opportunity to evaluate the risk characteristics that make one route preferable to another, namely, the comparison of Routes 86 and 111 -- both of which can access the site from the I-10 for trucks originating in the L.A. metropolitan area.

4.1 CHARACTERISTICS OF THE IT CORPORATION WESTMORLAND SITE

The IT Corporation Westmorland site is located 4 miles north-west of the City of Westmorland. Access is from Rt. 86 and Garvey Road and by a private IT Corp. paved road. The 1.5 mile access road extends from Rt. 86 at Garvey Road. It is approximately 190 to 210 miles from the center of the L.A. metropolitan area. The site can dispose of a maximum of 87,360 tons per year of "non-geothermal" Group 1 wastes and approximately 500,000 tons per year of geothermal wastes.

4.2 TRUCKLOAD VOLUMES GENERATED BY THE IT WESTMORLAND SITE

Information from environmental documents showed that the site accepted an average of 9 truckloads/day of non-geothermal wastes and the site will generate a maximum of 44 trips per day. However, staff felt that due to the more aqueous nature of Group 1 wastes, and more in keeping with the regional average, a factor of 15 tons/load was more representative. This would adjust truckloads generated to an annual average of 16 truckloads/day and a maximum of 29, or 58 trips per day (based on the monthly restriction).

4.3 COLLECTION AND ANALYSIS OF ACCIDENT DATA

Rates were obtained from Caltrans (TASAS) for detailed segments of routes 86 (from Jct. 111 to Mexican Border) and 111 (Jct. I-10 at West Palm Springs Village to Mexican Border). The data allowed an analysis of accidents (for all types of vehicles) on Rt. 86 (the main access route), as well as a comparison of 86 to 111 (as an alternative).

Based on standards previously developed, segments exhibiting an overall accident rate above the statewide average were identified. It is assumed that a rate of 5.0 acc/MVM (for all types of vehicles) represents the statewide average for a 2-lane conventional undivided rural highway (please see the above full study report for details.

In our hypothetical comparison of access routes to the IT Corp. Westmorland site populations potentially at risk were also estimated. Even though in almost all cases, truckers use Rt. 86 and not Rt. 111, it is assumed for purposes of demonstrating this methodology, that Rt. 111 is a viable alternative.

4.4 SUMMARY OF FINDINGS

Analysis results clearly showed that Rt. 111 has a much higher risk index than Rt. 86 (151,000 to 46,000 or 3.3 times greater risk). Extremely high accident rates in Coachella and Calipatria greatly increase the risk factor over that of Rt. 86. These results simply mean that based on highway accident history, and surrounding population, the risk--in terms of probability and magnitude of exposure to hazardous waste materials--appears to be 3.3 times as great on Rt. 111. Rt. 86 may present traffic hazards at certain commercial centers, but compared to Rt. 111 its risk index is certainly more favorable.

The number of hazardous waste trucks that are expected to access the IT Westmorland site is small. The safety record of the local streets and roads in the vicinity of the City of Westmorland and the site itself is excellent. Given these facts, the impact on public safety when transporting hazardous wastes to the IT Westmorland site, did not appear to be significant.

6.0 RISK INDICES FOR ROUTES IN SAN DIEGO AND SANTA BARBARA COUNTIES

In accordance with the study area of the Southern California Hazardous Waste Management Project, risk indices were obtained for all major routes in the in the 8-county study region. Consequently SANDAG and Santa Barbara County - Cities Area Planning Council performed similar route risk analyses under contract with SCAG (please see the above full study report for

details).

Detailed accident data, vulnerable populations and sensitive ecological areas on and surrounding routes were supplied by the Santa Barbara County--Cities Area Planning Council.

Their analysis clearly showed that of 3 alternative routes analyzed, one had a very low index in comparison to the other two (1/8 of the next lowest alternative). Similar to the findings of the BKK Wilmington Treatment Facility and IT Corporation Westmorland analyses, the risk assessment methodology used indicates a clearly preferred route for transporting hazardous wastes. The Santa Barbara County--Cities Area Planning Council identified the following preferred route (from the three alternatives): Leaving Rt. 101 at Los Alamos (common freeway egress point) to Rt. 135, to Rt. 1, north to Black Road.

Similar information supplied by SANDAG for 11 freeway and 1 non-freeway highway links in the San Diego region was supplied. Risk indices were derived for each link (including Rt. 67 accessing the BKK Chula Vista Treatment Facility) and then prioritized on a "best to worst" basis. The SANDAG report summarized data for all these links and clearly presented freeway transportation safety data required for the siting of future hazardous waste disposal facilities, and for access to the existing BKK Chula Vista facility.

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(1) Southern California Hazardous Waste Management Project. Transportation of Hazardous Waste. SCAG. February 1985.

Southern California Hazardous Waste Management Project. Potential for Hazardous Waste Transport by Rail. SCAG. January 1985.

* Copies of these reports can be obtained from:
Lawrence Black. SCAG. 600 S. Commonwealth Ave. Los Angeles. CA 90005 (213-739-6680).

(2) Guidelines for Applying Criteria to Designate Routes for Transporting Hazardous Materials. Federal Highway Administration. Nov. 1980, Section II, Risk Determination.

(3) Draft EIR. 45-82-SUB. SCH NO.82043006. Appropriate Technologies 1. Industrial Liquid Waste Treatment and Transfer Facility (AP-TEC 1). BKK Corporation, Wilmington. California. Lockman and Associates, January 1983.

(4) "Percentage Trucks of Total Traffic Volumes". Highway Log. Caltrans, 1981.

(5) Establishing Routes for Trucks Hauling Hazardous Materials in Portland, Oregon, City of Portland Office of Emergency Management. January, 1984.

RISK ANALYSIS AND RISK MANAGEMENT
METHODS FOR ENVIRONMENTAL LIABILITIES

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Definitions

Risk Analysis: Using quantative techniques and/or expert scientific opinions to establish the amount of risk of health or environmental damage which exists or which could exist under varying scenarios.

Risk Management: The process of evaluating risk and initiating such actions as to reduced these risks.

Environmental Liability: The financial and legal consequences a party may occur as a result of an event which affects the environment and/or human health

Loss Control: Those services designed to minimize the finacial loss and environmental impacts associated with a environmental exposure opportunities.

Current Status:

Changing Regulatory Climate With Focus On Hazardous Materials Management

(a) Increased controls on storage and transport and disposal (RCRA)
(b) Classification of materials as hazardous (RCRA)
(c) Increased monitoring and reporting requirements (RCRA)

(d) Regulations on air Toxics (Clean Air Act)
(e) Information to employees and customers (OSHA/MSDS)
(f) Pre-manufacturing notification (TSCA)
(g) Toxicological reviews and reporting (TSCA)
(h) Transport safety (DOT)/State

Changes in Analytic Technology

Toxicology Regulations

kg gr mg μg, ng pg fg

Analytic

Changes in Legal Environment

(1) Damages
(2) Trebble damages
(3) Apportionment
(4) Deep pockets
(5) Roll of hold harmless

Changes in Insurance (large Losses) - 3-4 Billion 1985

(a) Termination of pollution liability coverage sudden and accidental as well as long term
(b) Formation of captives
(c) Non-severability
(d) Claims made policies
(e) Corporate going bare

Impacts of Above Changes

(a) Assets unprotect
(b) Losses come directly out of profits
(c) Self insurance

(d) Legal fees now 25-30% of total cost of settlement

These changes have created a diffcult situation for both government and industry.

Tools to be used to provide guidance in this difficult environment include:

(Risk Assessments)

(1) Audits/Surveys
  (a) regulatory compliance
  (b) permit
  (c) internal policy and procedure
  (d) real estate/corporate transaction

<u>Health Risk Assessments</u>

(a) Exposure assessments (retrospective)
(b) Exposure assessments (prospective)
(c) Expert toxicological evaluations
(d) Toxicological pathway analysis

<u>Industrial Hygiene Surveys</u> - Worker Exposure Issues

<u>Remedial Investigations</u>

<u>Quantative Engineering Assessments</u>

(a) Probabilistic stastical programming
(b) FAult tree analysis
(c) Haz-OP analysis

<u>Methods to help minimize losses and liability</u>

(1) Hazardous materials handling - training
(2) Emergency Loss Control
(3) Follow up on correction of deficiences found in Risk Assessment exercises
(4) Preventive maintenance scheduling
(5) Policy and procedure developing
(6) Self auditing to assure compliance with P&P

Major Offenders

(a) Poor training of employees
(b) Leaking tank
(c) Inappropriate use of equipment
(d) Faulty equipment

Conclusion:

Continuing changing environment with strong social/legal pressure with large unprotected financial liabilities require reliance of the latest methods to use for early detection and prevention of problems. If problem occurs need to focus on rapid emergency response technical services to minimize losses.

A RISK ANALYSIS APPROACH TO "HOW CLEAN IS CLEAN?"

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"HOW CLEAN IS CLEAN?"

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ABSTRACT

A methodology is described and demonstrated, in the context of a realistic hypothetical example, for determining remedial action criteria for contaminated soil. The methodology addresses in a quantitative and organized way the key factors involved in deciding "how clean is clean?". The approach is based in risk analysis and quantifies the tradeoff between extent (and cost) of remedial action and demonstrated degree of certainty in achieving an adequate level of health protection.

Standard site characterization information is used to develop models for source-to-receptor processes for important potential exposure pathways. The transport and pathways models are used to back-calculate the concentration of contaminant in the soil required to assure that exposures are below an acceptable safe threshold for exposure or risk. Uncertainties about key processes and parameters are treated quantitatively using probabilistic techniques and are propagated through the model. The result is a quantification of the tradeoff between the extent of remedial action (as indicated by "safe" soil concentration for each pathway) and the probability that the soil concentration will result in "safe" exposure levels given the uncertainties involved.

The methodology is applied using realistic data for a typical site contaminated with PCB's and chromium. Three potential exposure routes are examined: (1) soil resuspension and inhalation, (2) crop uptake and ingestion, and (3) groundwater contamination and subsequent drinking water ingestion. The relative importance of each pathway with respect to risk contribution is determined along with the level of certainty that various soil concentration criteria will result in acceptable exposures from each pathway. The results have useful implications for selecting appropriate remedial actions, provide a more defensible basis for recommended action, and can be used to help assure that a consistently high degree of public protection is obtained without over- or under-spending at any given site.

INTRODUCTION

Subpart F of the National Contingency Plan (NCP)[1] for oil and hazardous substances outines the required steps for responding to a hazardous substance release under CERCLA. This seven phase approach covers all aspects of the response from discovery and notification through documentation and cost recovery. Phase six requires a detailed remedial investigation and feasibility study (RIFS) of alternative actions for the site to "prevent or mitigate the migration of a release of hazardous substances into the environment." Through a detailed analysis of the alternatives, including the no action alternative, the effectiveness of the remedial actions can be compared in terms of minimizing both adverse environmental impacts and costs. The alternative selected must meet the guideline of being "the lowest cost alternative that is technologically feasible and reliable and which effectively mitigates and minimizes damage to and provides adequate protection of public health, welfare, or the environment." For contaminated soils, this guideline assumes a knowledge of what concentration will meet the "adequate protection" requirement. The acceptable concentrations are dependent on the types and quantity of substances at the site along with the pathways that could lead to population exposures.

These factors are evaluated qualitatively in the preliminary rating of the site using the Hazard Ranking System model[2]; in order to make decisions on actual cleanup levels it is necessary to quantify the tradeoff between extent (and cost) of remedial action and demonstrated degree of certainty that an adequate level of environmental protection will be acheived by that action. This paper presents a risk assessment methodology that determines acceptable soil concentrations based upon a contaminant's toxicity (characterized by a daily acceptable intake rate derived from standards and criteria) and the contaminant's ability to be taken in by people near or onsite (described by using exposure pathway modeling).

Such an analysis provides a reasonable and defensible basis for recommended remedial actions which accounts for important uncertain factors in the source-to-receptor pathways in such a manner that tradeoffs between the cost and the level of protection afforded by a recommended action can be explicitly addressed. Because every hazardous waste site has unique environmental and contamination characteristics, it was felt that the best way to illustrate our quantitative assessment method was to provide a site specific hypothetical example.

SALIENT CHARACTERISTICS OF THE HYPOTHETICAL SITE

The site is located in farmland with geologic and climatic conditions typical of the coastal plain of the Northeastern region of the United States. A schematic of the site is shown in Figure 1. The

area of contamination, which measures 135m by 125m overlies an aquifer of 10m depth. The unsaturated soil zone is approximately 5m deep, and contamination has been measured down to the water table. The contaminants detected were PCBs and chromium (Cr), and the vertical soil concentration profiles for each substance are shown in Figure 2. There is a well field in the aquifer downgradient from the site which draws 527 l/day supplying 25 people. There is no surface water near the site.

For the purpose of this example and for simplicity, it was assumed that there are only three possible exposure routes where onsite contamination would contact people. These pathways are:

1. inhalation of resuspended contaminated soil,
2. ingestion of crops grown in the contaminated soil and
3. drinking water from the well field downgradient to the site.

GENERAL METHODOLOGY

A. Determining Safe Doses

The first task undertaken is the development of a safe dose for the chemical species of interest. The safe dose, expressed in terms of mass ingested per unit body mass per year, is the level at which it is assumed that human health is adequately protected. Without a safe dose, no health criteria for the substance can be established for any medium, be it soil, air or water. For the purpose of this example, safe intake rates, expressed in mg/kg-yr, were derived from existing water criteria. The safe intake rate for chromium was derived from the EPA drinking water standard (0.05 mg/l), and the PCB intake rate was derived from the EPA water quality criterion (0.79 ng/l).

The safe intake rate for chromium (.521 mg/kg-yr) was calculated using the equation in Table 1, which assumes that a person's source of drinking water contains Cr at the drinking water standard. The safe intake rate for PCBs was calculated to be .0086 mg/kg-yr. This value was derived from the PCB water quality criterion which is based on the assumption that the critical pathway of exposure to PCBs in water is through the consumption of fish (see equation in Table 1). Specifically, the criterion was developed assuming a PCB reconcentration factor of 31,000 in fish and assumes that 24 kg of contaminated fish is eaten per year.

Other sources of data for the estimation of safe doses include the acceptable daily intake standards developed by the World Health Organization[3] and threshold limit values (TLV) established by the American Conference of Government Industrial Hygienists.[4] For compounds that do not have established limits, bioassay data may be used in conjunction with safety factors[5] to convert to safe human doses. For carcinogens that do not have established limits, safe doses must be

calculated which result in an acceptable cancer risk, since dose criteria are given in terms of cancer risk (eg, 10^{-6}/yr).

B. Pathway Models

In order to relate a safe dose to soil concentrations, models must be developed which simulate the transport of the substance from the source to the receptor population for each of the pathways of interest. For this example, each pathway has been modelled as a series of distinct environmental compartments with the contaminant in equilibrium between compartments. Figure 3 is a flow chart of the three models showing each of the compartments and the processes which control the movement of the contaminant from one compartment to the next. Each of the pathways can be expressed as a series of algebraic equations which are solved backwards to calculate the distribution of maximum allowable soil concentrations which will result in an acceptable dose. Tables 2-4 list the equations, assumptions and parameter distributions used to calculate the probability distributions for the safe soil concentrations for each pathway for PCBs and Cr.

C. Quantifying Uncertainty

There are significant uncertainties inherent in the calculation of risks associated with human exposures from uncontrolled hazardous waste sites. Even so, a decision maker must allocate resources for remedial action in a manner that provides reasonably high confidence that the public will be protected. The NCP requires that the remedial action chosen for a site be the most cost-effective alternative that meets the criteria of adequately protecting health. These remedial alternatives are designed to mitigate adverse health effects identified by the pathway analysis.

Both the pathway models and the input data to these models contain assumptions and estimates leading to results that are highly uncertain. Inputs such as windspeed and direction as well as the direction and rate of groundwater movement are variable over time and influence dose. Other inputs such as permeability may vary over the areal extent of the site. One way of treating this variability is the use of "best estimate" median values for the input variables. This may result in an unacceptable level of health risk if the variance of the model results is high since in this case the median will predict a safe soil concentration that could result in unsafe exposures. At the same time, use of conservative "worst case" estimates may result in the selection of alternatives that expend large amounts of capital in return for a minimal increase in health protection. A third technique, which is discussed below, uses stochastic modelling to develop a distribution of safe soil concentrations which examines the range of possible outcomes.

TABLE 1

EQUATIONS AND PARAMETERS USED TO DETERMINE SAFE DOSE RATES FOR Cr AND PCBs

<u>Cr</u>

Equation:

$$AD = \frac{DWS \times Uw \times 365}{70}$$

Parameters:

AD = Acceptable dose rate $\left(\frac{mg}{kg\text{-}yr}\right)$

DWS = Drinking water standard for Cr, 0.05 mg/l

Uw = Drinking water consumption rate, 2 l/day

365 = Conversion from days to years (day/yr)

70 = Weight of adult body (kg)

<u>PCBs</u>

Equation:

$$AD = \frac{WQC \times BAF \times Uf}{70}$$

Parameters:

AD = acceptable dose rate $\left(\frac{mg}{kg/yr}\right)$

WQC = water quality criterium for PCBs, 7.9E-7 mg/l

BAF = bioaccumulation factor from water to fish, 31,000

Uf = yearly consumption rate of fish (kg/yr), 24

70 = weight of adult body (kg)

TABLE 2

EQUATIONS, PARAMETERS AND ASSUMPTIONS USED TO CALCULATE SAFE SOIL CONCENTRATIONS FOR Cr AND PCBs - INHALATION OF SUSPENDED SOIL

Equation:

$$SCS = \frac{AD \times BM}{SPC \times 0.75 \times BR \times IAF \times 10^{-6}}$$

Parameters:

SCS = maximum acceptable soil concentration ($\frac{mg}{kg}$)

AD = Acceptable dose rate ($\frac{mg}{kg\text{-}yr}$)

BM = bodymass (Kg)

SPC = concentration of ambient airborne particles (mg/m^3)

0.75 = factor converting total airborne particles to suspended soil

BR = breathing rate (m^3/yr)

IAF = fraction of inhaled substance absorbed into the blood

10^{-6} = unit conversion

Assumptions:

1. Suspended particles have same contaminant concentration as site soil.
2. Exposure is for 24 hours per day, 365 days per year
3. Particle median aerodynamic diameter is 1 micron.
4. No contaminant loss process

TABLE 3

EQUATIONS, PARAMETERS AND ASSUMPTIONS USED TO CALCULATE SAFE SOIL CONCENTRATIONS FOR Cr AND PCBs - INGESTION OF SITE GROWN CROPS

Equation:

$$SCR2 = \frac{AD \times BM}{CI \times CCF \times GAF}$$

Parameters:

SCR2 = maximum acceptable soil concentration $\left(\frac{mg}{kg}\right)$

AD = Acceptable dose rate $\left(\frac{mg}{kg\text{-}yr}\right)$

BM = bodymass (Kg)

CI = ingestion rate for crops $\left(\frac{mg}{kg\text{-}yr}\right)$

CCF = soil to plant concentration factor

GAF = fraction of ingested substance absorbed into the blood

Assumptions:

1. All plant matter consumed derived from site grown produce
2. No contaminant loss processes
3. No irrigation of crops with contaminated groundwater

TABLE 4

EQUATION, PARAMETERS AND ASSUMPTIONS USED TO CALCULATED SAFE SOIL CONCENTRATIONS FOR Cr AND PCBs - DRINKING OF GROUNDWATER

Equation:

$$SCMAX = \frac{AD \times BM \times VGW}{SWPF \times VL \times WI}$$

Parameters:

SCMAX = maximum acceptable soil concentration $\left(\frac{mg}{kg}\right)$

AD = Acceptable dose rate $\left(\frac{mg}{kg\text{-}yr}\right)$

BM = bodymass (Kg)

VGW = flow of uncontaminated groundwater diluting the contaminated leachate (l/yr)

SWPF = soil to water partition factor

VL = flow of leachate (l/yr)

WI = water ingestion rate (l/yr)

Assumptions:

1. VL is net infiltration times surface area (125 x 135 m)
2. Equilibrium is assumed between soil and water contamination
3. No loss, attenuation or dispersion processes assumed
4. The leachate is diluted only by the flow of water pumped out of the aquifer

In order to analyze the uncertainty in each pathway model, the inputs were specified as probability distributions and propagated through the model using Latin Hypercube sampling (LHS) with random pairing of the inputs. The advantage of using LHS over standard Monte Carlo sampling is that it forces sampling of the entire range of input distributions, reducing the number of samples required. Besides sampling over the range of input values, LHS is preferred to other sampling techniques in that it is an unbiased estimator of the cumulative density function and mean for the output variables. While the estimate of variance is biased, it has a lower mean square error than comparable sampling techniques. These properties hold true for models where the output is a monotonic function of the inputs, as is the case with the pathway models presented in this paper. The properties of LHS are addressed in detail by McKay, Conover and Beckman(6) and Iman, Helton and Cambell(7). LHS is especially useful in problems using models that are very complex or that use inputs that have a very large variance since it reduces computer costs.

Developing technically sound, defensible probability distributions for the input parameters is the most important phase of the risk analysis approach described in this paper. If there is a sufficient source of data for the variable, statistical techniques may be used to fit the data to an appropriate distribution. If the data is erratic and does not fit any standard distribution, the cumulative density function (CDF) may be input directly into the model as a user specified distribution.

For most remedial investigation and feasibility studies of hazardous waste sites, much of the data required to generate input distributions will be missing and will require the use of well informed expert judgment to develop subjective probability distributions for the input data. Developing these distributions requires the use of formal elicitation procedures which are designed to overcome common heuristics and biases often inherent to the expert's probability estimates.(8) This requires interaction between the expert, the pathway analyst and a professional trained in elicitation procedures. The procedure forces the expert to make a more considered estimate which leads to a more defensible model. Table 5 lists the models inputs and distributions developed for each.

Appendix A provides the basis for each parameter distribution. Due to the fact that the purpose of this paper was to illustrate a methodology, extensive effort was not expended in developing the model parameter distributions. It should be understood that these distributions only represent a first cut approximation based upon the expertise of the authors. It is important to note that uncertainty analysis is not a panacea, but serves to maximize the use of available knowledge and give the decision maker additional information on the degree of confidence in a particular remedial measure. The results of

the uncertainty analysis may also indicate the need to collect more data before an informed decision can be made.

RESULTS AND DISCUSSION

A. Defining Remedial Objectives

The basic result of the methodology is a distribution of soil concentrations vs the cumulative probability that the soil concentration is safe (yields a safe intake of Cr or PCBs through a given exposure pathway). Figures 4 and 5 show the results of the pathway analyses for PCBs and Cr plotted as a complementary cumulative density function (CCDF). The abscissa is the log maximum allowable contaminant concentration in the soil. The ordinate is the probability that a given soil concentration will result in an exposure equal to the acceptable rate. The plot is read by picking a desired confidence level and reading off the corresponding soil concentration.

Also indicated on each figure is the maximum soil concentration measured at the hypothetical site. This concentration is the relevant comparison point for the drinking water pathway. For the inhalation pathway, safe soil concentrations should be compared to site specific concentrations at the surface and the crop pathway should be compared to maximum concentration in the root zone, ie, the top 0.5 meters. As shown for Cr (Fig 5), there is a 100% probability that the maximum soil concentration at the site is unsafe through the groundwater pathway. Similarly, Figure 4 shows that there is a 95% probability that the maximum PCB soil concentration is unsafe through the ingestion of groundwater. There is a 15% chance that the maximum chromium level is unsafe through the crop pathway and there is a 60% chance that the PCB crop pathway will lead to an unacceptable dose. Note, also, that there is no chance that the levels of chromium or PCBs are unsafe through inhalation of resuspended soil.

The information depicted in our resulting distributions indicate the remedial objectives for this site even when significant technical uncertainties exists. Any remedial action chosen for this site must prevent or mitigate the migration and exposure through the ingestion of crops grown onsite and the ingestion of groundwater from the underlying aquifer, given that probabilities of unsafe doses discussed above exceeds the required confidence level to provide adequate protection. If the acceptable level of confidence in insuring a safe dose was 80%, there would be no need to control the intake of chromium from the crop pathway since there is a 85% chance that the dose will be below the acceptable limit.

TABLE 5

INPUT DISTRIBUTION FOR THE PATHWAY MODELS

Variable	Description	Units	Distribution
BM	Body Mass	Kg	3 Point (2,40,120)
CI	Crop Ingestion	Kg/yr	Uniform (100,400)
BR	Breathing Rate	m^3/yr	Uniform (3650,10950)
WI	Water Consumption	L/yr	Uniform (365,1095)
SPC	Conc Suspended Soil Particles	mg/m^3	Normal, $\bar{X}$ = .025,SD = .01
VL	Leachate Volume	L	Uniform (843750,4218750)
GAF	Gut to Blood Transport Factor	-	PCBs Loguniform (.001, 1) Cr Loguniform (.0001,.1)
IAF	Lung to Blood Transport Factor	-	PCBs Loguniform (.01,1) Cr Loguniform (.01,.60)
CCF	Soil to Crop Partition Factor	-	PCBs Loguniform (1E-5,1) Cr Loguniform (.001,0.1)
SWPF	Soil to Water Partition Factor	-	PCBs Loguniform (1E-6,IE-4) Cr Loguniform (.0001,.01)
VGW	Volume Ground Water	L	Fixed 192500
AD	Safe Dose of Substance	(mg Substance/ kg body mass - yr)	PCBs .0086 Cr .52

B. Impact of Uncertainty

Both Figures 4 and 5 show that the distribution of soil concentrations over the range of 0 to 100 percent probability of acceptable dose have a high variance. The crop pathway spans over five orders of magnitude and the drinking water and inhalation pathways span over three orders of magnitude. This indicates that selecting a remedial action based on the median value of the soil concentration could lead to a dose above the maximum allowed. This can easily be shown by substituting in a soil concentration from the median and the tail of the distribution and solving the pathway models for dose.

Figure 6 shows the distribution of dose for soil concentrations at the median and 95th percentile for the PCB drinking water pathway. If the remedial action treated the soil to a concentration of 4 ppm, there would be a 50 percent chance of exceeding the allowable dose and a 25 percent chance of exceeding the dose by a factor of three. Treating the soil to 0.2 ppm would reduce the chance of exceeding the dose limit to 5 percent. Another important comparison to be made with the results of this analysis is to examine the use of a worst case estimate procedure. In order to adequately protect health, this type of analysis is often performed using conservative worst case estimates for the input variables. This would be analogous to using values from the tails of the current input distributions. This analysis was performed for the PCB crop pathway using the values from the 10 percent trails for MASS, CROP, GAF and CCF. Using these values, the maximum soil concentration calculated was .001 ppm.

Compared to the plot for the crop pathway in Figure 4, this lies outside the range of data. This results from the fact that the probability that all the variables would be in that part of the tail is very slight. Protection to this level would not be cost effective since the compounding of independent events with correspondingly low probabilities results in a very rare occurrence. While the result would be all adequate protection of health, it might only be achieved at unnecessarily high cost, depending on the remedial action. The range in these results indicates that selecting an acceptable level of uncertainty will impact the design of remedial alternatives.

Continuing with the example of the PCB crop pathway, the impact of the uncertainty on choosing remedial alternatives can be illustrated. Given the PCB concentration of 75 ppm for the root zone at this site, both the best estimate and worst case analyses would indicate the need to control the crop pathway since they predict maximum safe soil concentrations of 14.7 and .001 ppm, respectively, which exceed the measured concentration. For this site, if PCB's were the only contaminant, two types of control technologies might be used.

The first are treatment technologies such as incineration and chemical or biological degradation which can result in a continuum of removal efficiencies which vary with cost. For these technologies, the higher the removal efficiency, the greater the cost. Using the best estimate, there will still be a significant (50%) probability that there will be health risks from treating to 14.7 ppm. Treatment to .001 ppm will provide certain protection of health but will cost more than treatment to the 95% confidence limit of .01 ppm which can also provide adequate protection, but more efficiently.

The second class of control technologies are ones such as capping which do not usually result in a continuum of treatment efficiencies. For this site, all three analytical technologies would trigger the control technology. There could be cases, however, in which the use of the best estimate or worst case analyses would result in an inefficient use of cleanup funds. For this case, consider a soil concentration of 10 ppm. The best estimate procedure would indicate that this would be a safe level, when in fact there is considerable uncertainty of protecting health. The methodology presented in this paper would show that the soil concentration of 10 ppm in not safe. Likewise, if the measured concentration was .01 ppm, the worst case analysis would indicate that the pathway would need to be controlled. Our analysis indicates that a soil level of.01 ppm would in fact result in a high probability of a safe dose, eliminating the need to control the pathway.

The above discussion illustrates how the design of remedial alternatives can be dependent on the level of confidence associated with the protection of health. Before proceeding with the remedial design stage, it is useful to perform an informational analysis designed to identify key data gaps and determine what additional data should be collected to reduce the uncertainty.

C. Sensitivity Analyses

The objective of collecting additional data is to reduce the uncertainty in the model results. The first task in determining which, if any, additional data should be collected is to rank variables according to their contribution to the model variance. If one or two variables account for a majority of the model variance, the gain in collecting data on the other variables will be insignificant. By performing sensitivity analyses on the results, the input variables may be ranked by their contribution to the overall model variance.

Figure 7 illustrates how the spread in the results varies as each input is fixed to its median value. With none of the input distributions fixed, the spread ranges from -2.6 to 4.8, over 7 orders of magnitude. By fixing the value of GAF to its median, this spread is reduced by a factor of ten. When the value of CCF is fixed to its median, the spread is reduced by a factor of 1000. Obviously, reducing

the variability of either input would reduce significantly the variance of the results.

Table 6 lists the results of the sensitivity analyses for each of the pathways. The "scores" for each variable were calculated as the ratio of the variance of the result with the variable fixed to the variance of the result with that variable (and all others) defined by their input distributions. The variance was measured as the difference between the 10th and 90th percentiles. This ratio measures the contribution of the variable to the overall model variance; the lower the score, the greater the contribution of that variable to the overall variance. Other, more rigorous techniques are available for performing sensitivity analyses, but the scope of this paper prevents their presenttion. The interested reader should refer to the work of Iman, Helton and Cambell[7] for a discussion of these techniques.

Once the variables have been ranked in this manner, it is easier to identify where additional data should be gathered. Looking at each of the pathways in Table 6, it is evident that the variance in the partition factors contribute the most to the overall model variance. Reducing the uncertainty in the other variables such as population characteristics will not significantly reduce the uncertainty in the results unless the partition factors are more accurately defined.

The value of additional information should be balanced against the cost of the data. As noted above, unless the uncertainty of the partition factors is reduced, collecting other data would not be cost-effective. Collecting data for the inhalation pathway would not be useful since Figures 4 and 5 indicate there is no need to control inhalation from a human health risk standpoint. Cost-effective data collection strategies for this site may include experiments to determine the soil water partition factor and the rate of contaminant uptake into plants. If new data were collected, the analysis would be redone to determine if collecting data on the remaining variables could now increase the precision of the model.

D. Identification of Remedial Action Alternatives

Once the remedial objectives are defined, the process to identify viable remedial action alternatives is initiated. For this hypothetical case the remedial objective is to alleviate to acceptable levels environmental risk due to soil Cr and PCBs for the crop and groundwater pathways. All remedial action alternatives must then prevent or mitigate these two pathways. Table 7 lists a representative number of possible remedial alternatives and indicates whether or not each

TABLE 6

SENSITIVITY ANALYSIS RESULTS

Pathway	Variable	PCBs		Cr	
		Rank	Score	Rank	Score
Crop Ingestion	BM	3	.98	3	.94
	CI	4	1.0	4	.97
	CCF	1	.52	1.5	.82
	GAF	2	.89	1.5	.82
Drinking Water	BM	2	.89	2	.94
	SWPF	1	.66	1	.61
	VL	3	.96	3	.998
	WI	4	.97	4	1.0
Inhalation	BM	2	.84	2	.78
	BR	4	.99	4	1.0
	IAF	1	.63	1	.62
	SPC	3	.98	3	.91

alternative meets the objective. As indicated in the table, three out of the seven alternatives fulfill the objective. These alternatives are:

1. solidification,
2. capping,
3. removal with disposal or destruction.

Given the fact that solidification requires extensive testing, the two most viable remedial alternatives for this site would be removal or capping.

CONCLUSION

This analysis shows that due to the uncertainty in the models and inputs, a quantification of risk is essential to selecting an effective remedial action. While there has been much attention focused on assessing the risk of exposure to hazardous substances, little effort has gone into assessing the uncertainty associated with the occurrence of exposure. This paper points out that assessing exposure levels is highly uncertain and requires the utilization of quantitative uncertainty analysis.

The use of median valued or worst case estimates can lead to an inefficient allocation of cleanup funds. With median valued estimates, funds can be spent without achieving an adequate protection of health while a worst case analysis may require the expenditure of excess funds that do not result in an corresponding increase in health protection. A quantitative risk analysis approach to the problem explicitly addresses the question of uncertainty and gives the decision maker a look at the probable range of possible outcomes given the current state of knowledge. The results of this analysis, combined with sound engineering designs and cost analyses will result in a much more defensible selection of remedial alternatives.

TABLE 7

- REMEDIAL OBJECTIVES -

TO ALLEVIATE TO ACCEPTABLE LEVELS ENVIRONMENTAL
RISK DUE TO SOIL Cr AND PCBs FOR THE
FOLLOWING PATHWAYS

Remedial Alternative	Pathways		Remarks
	Crops	Groundwater	
No Action	No	No	
Onsite Treatment			
o Solidification	Yes	Yes	Extensive Testing Required
o Biological degradation	No	No	Would Not address Cr
Onsite Containment			
o Fencing	Yes	No	
o Capping	Yes	Yes	
o Run-off diversion	No	No	
Removal and disposal or destruction	Yes	Yes	

APPENDIX A

Technical Bases for Parameter Distributions

Contaminant Independent Parameters

1. Body Mass, Kg (BM)

It was assumed that the range of typical human body weights for all ages ranged from between 2 and 120 Kg with the median weight of about 40 Kg.

2. Crop Ingestion, Kg/yr (CI)

The recommended CI values listed in NRC Regulatory Guide 1.109[9] range from 190 to 240 Kg/yr for child, teen and adult age groups. Assuming that infants also consume vegetable matter and that a significant number of people are vegetarians the above range was extended from 100 to 400 Kg/yr. No attempt was made to specify any other probability values beside the minimum and maximum.

3. Breathing Rate, m^3/yr (BR)

The recommended range of BR values listed in NRC Regulatory Guide 1.109 for all age groups was utilized. No attempt was made to specify the distribution other than a uniform probability range.

4. Water Consumption, l/yr (WI)

The recommended range of WI values listed in NRC Regulatory Guide 1.109 for all liquid intake was used. Again a uniform probability range was assumed.

5. Concentration of Suspended Soil Particles, mg/m^3 (SPC)

Concentration data for total respirable particles throughout the rural US average about .035 mg/m^3 $\pm$ 0.01.[10] This distribution was assumed for this work, however the average concentration was reduced by 25% to account for the fact that soil represents about 75% of the total suspended dust load in rural areas[10].

6. Leachate Volume, l (VL)

Leachate volume is the product of infiltration times surface area of the site (125 x 135 m^2). The infiltration rate is based on the average annual rainfall for the northeastern US of 1 m/yr.[11] Infiltration ranges from 5 to 25 percent of rainfall, due to losses from

runoff and evapotranspiration.[12] The resultant range was from 843750 to 4218750 liter/yr.

Contaminant Dependent Parameters

1. Gut to Blood Transport Factor (GAF)

Cr - Depending upon the compound ingested ICRP 30[13] states that the gastrointestinal absorption of chromium can vary from 5×10^{-3} to 0.1 or more. We therefore assumed that the range of values for GAF could vary from 1×10^{-4} to 0.1. No attempt was made to refine the distribution from loguniform.

PCBs - It was assumed that the fraction of PCBs absorbed by the gut could be as little as 10^{-3} when ingested in a form absorbed to food or as much as 1.0 due to the lipid soluble nature of this substance. Again, a loguniform distribution was assumed.

2. Lung to Blood Transport Factor (IAF)

Cr - Maximum particle deposition in human lungs has been measured to be around 60% for respirable particle sizes.[14] The maximum Cr absorbed was considered to be 60% of the total inhaled Cr. Due to the insoluble nature of Cr^{+3} (the most prevalent valence state in the environment), the minimum amount inhaled that is transported to the blood was assumed to be 1%.

PCBs - No information was obtained concerning the amounts of inhaled PCBs reaching the blood. The range therefore was assumed to be between 1 and 100%.

3. Soil to Crop Partition Factor (CCF)

Cr - The range of CCF value reported in ORNL-5786[15] was used.

PCBs - No information was obtained addressing soil to plant concentration ratios for PCB. The majority of CCF for elemental forms range from about 10^{-5} to 1.0 (ORNL-5786). This range was employed for PCBs.

4. Soil to Water Partition Factor (SWPF)

Empirical soil to water partition factors, reported in or derived from the literature, were used. For PCBs, the partition factor may range from 10^{-4} to 10^{-6}, depending on the degree of chlorination of the PCBs (lower chlorinated PCBs partition less strongly to soil) and the organic carbon content of the soil[16,17,18]. For chromium, the partition factor will depend in part on the oxidation state of the

chromium, with CR (VI) being much less strongly adsorbed by soils then CR (III). The range selected (10^{-2} to 10^{-4}) covers that generally expected for both ions[19,20].

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FIGURE 1

SCHEMATIC DIAGRAM OF AN UNCONTROLLED HAZARDOUS WASTE SITE IN THE RURAL NORTH EAST

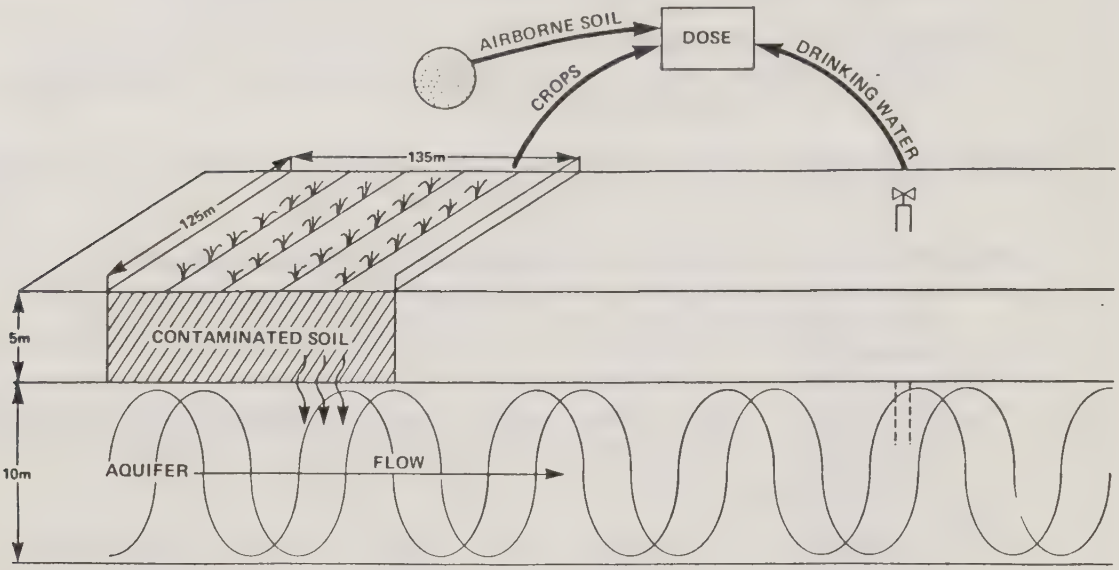
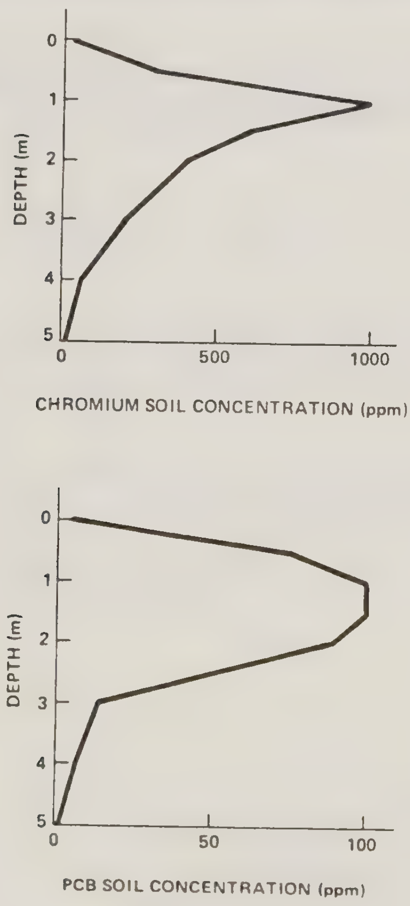


FIGURE 2

CONTAMINANT CONCENTRATION PROFILES



COMPARTMENTAL PATHWAY MODELS

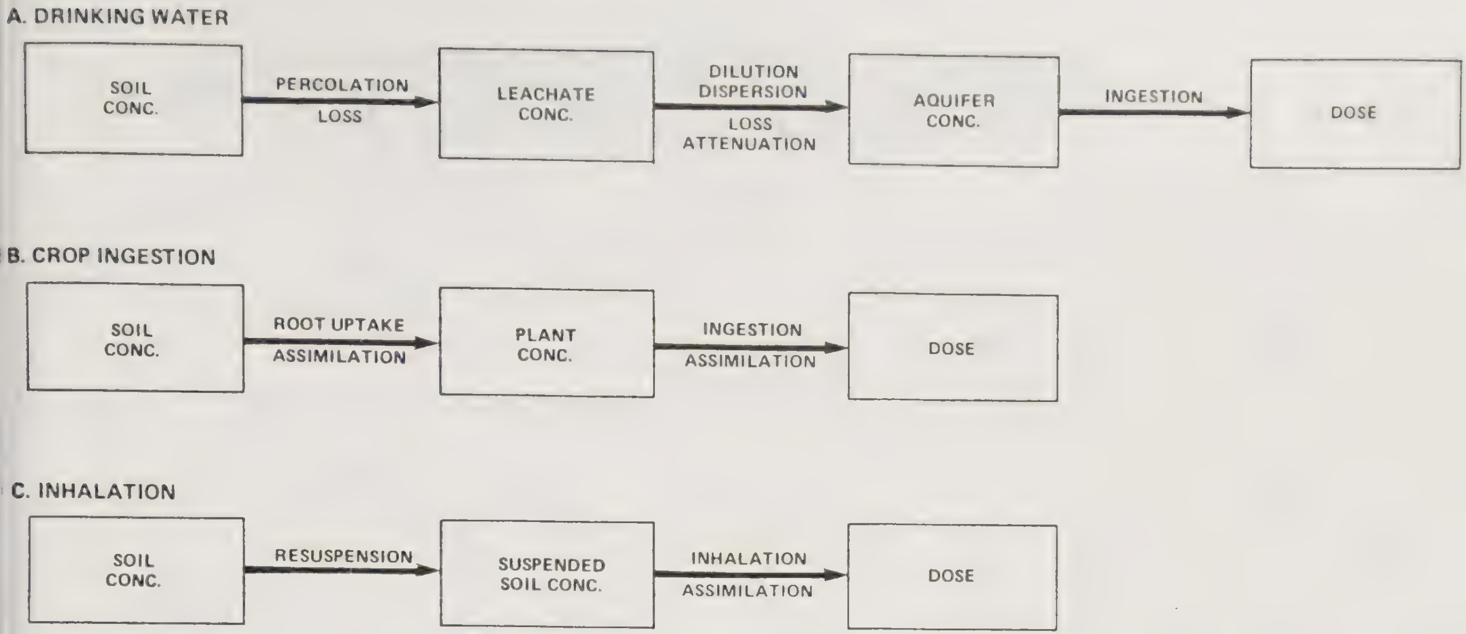


FIGURE 4

PROBABILITY DISTRIBUTIONS REPRESENTING DEGREE OF CERTAINTY THAT VARIOUS PCB SOIL CONCENTRATIONS WILL RESULT IN AN ACCEPTABLE DOSE LEVEL

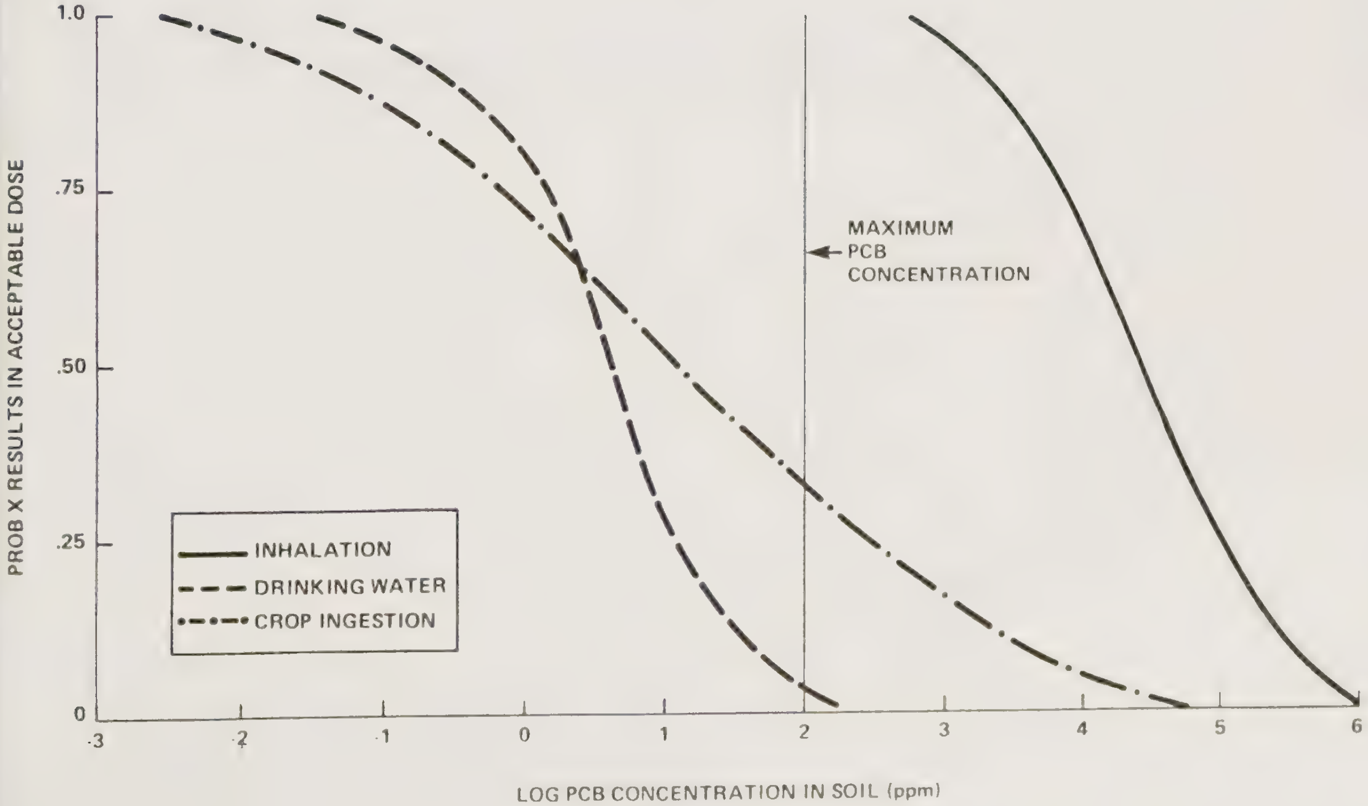


FIGURE 5

PROBABILITY DISTRIBUTIONS REPRESENTING DEGREE OF CERTAINTY THAT VARIOUS CHROMIUM SOIL CONCENTRATIONS WILL RESULT IN AN ACCEPTABLE DOSE LEVEL

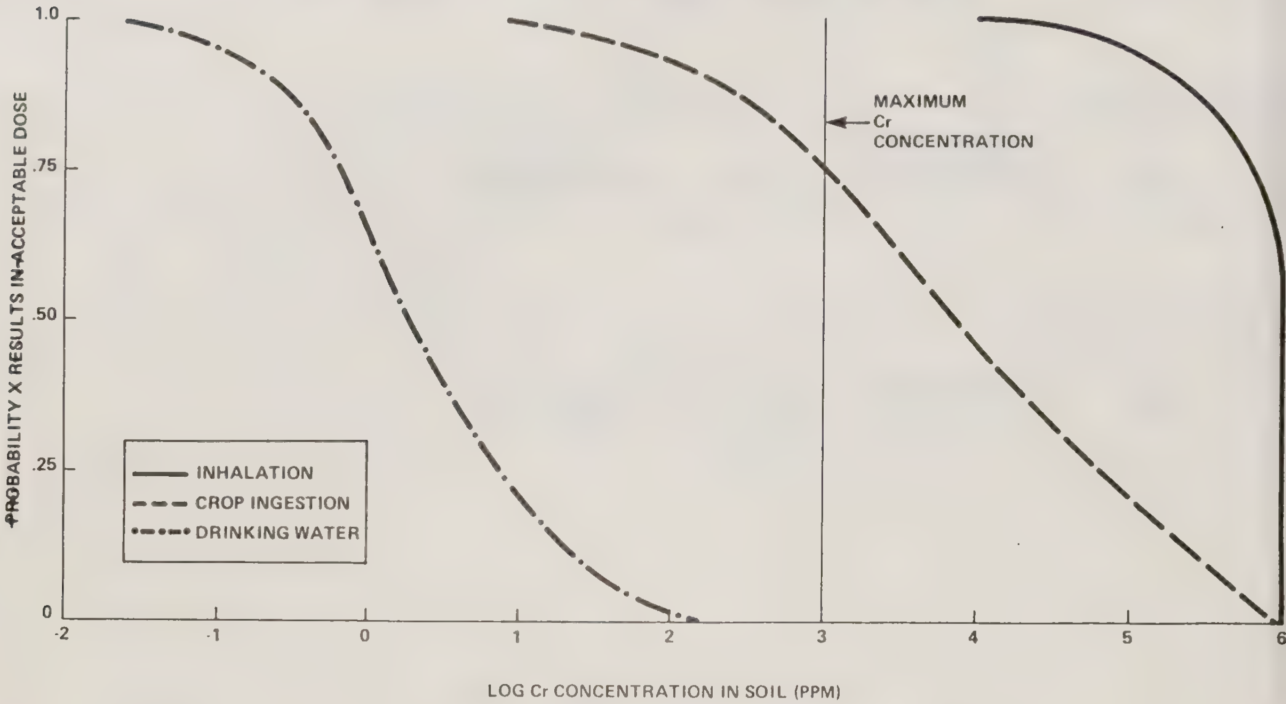


FIGURE 6

DOSE AS A FUNCTION OF RESIDUAL PCB CONCENTRATION DRINKING WATER PATHWAY

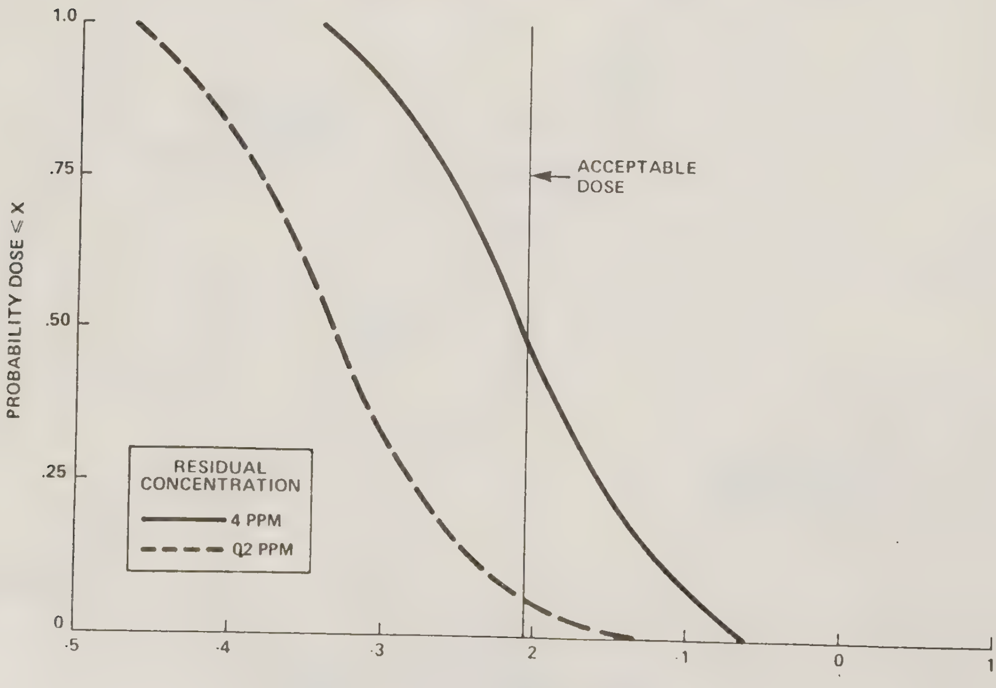
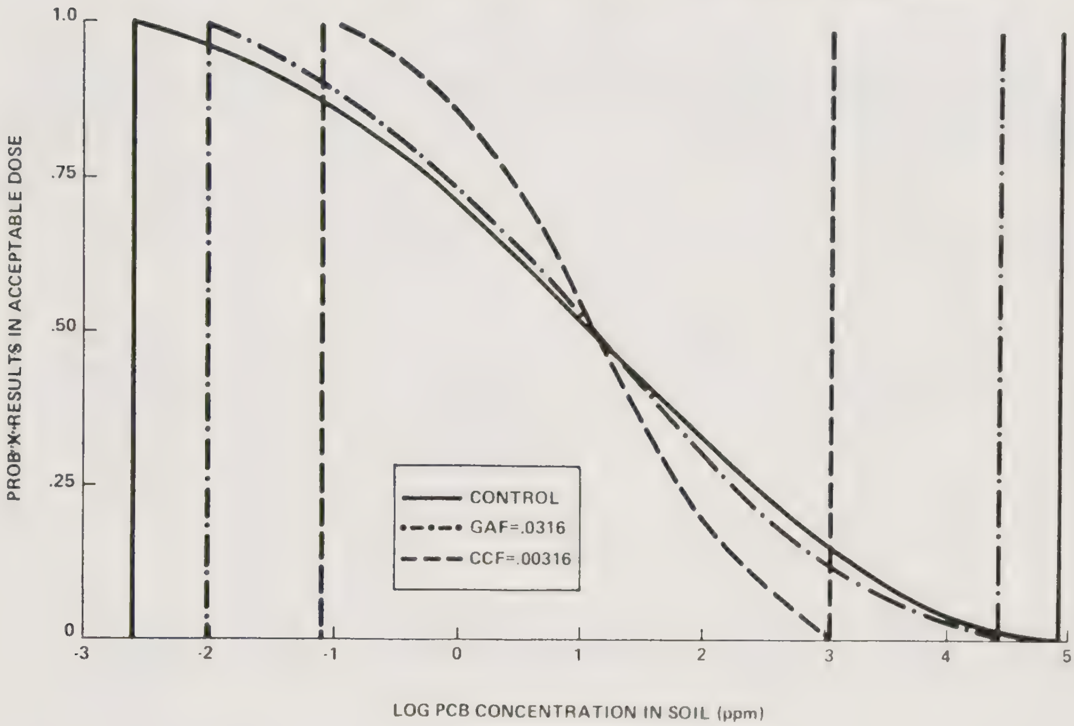


FIGURE 7

SENSITIVITY ANALYSIS EXAMPLE - PCB CROP PATHWAY



A PRELIMINARY SCREENING ANALYSIS FOR ESTIMATING ACCEPTABLE AIRBORNE TOXIC POLLUTANT EMISSIONS FROM MUNICIPAL SOLID WASTE INCINERATORS

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Abstract

A screening methodology is described and demonstrated for determining acceptable emission rates from municipal solid waste incinerators (MSWI). The methodology addresses in a quantitative and organized way the key factors involved in deciding acceptable emissions. The approach is based in risk analysis and quantifies the tradeoff between predicted emission rates and the demonstrated degree of certainty in achieving an adequate level of health protection.

Seven generic transport and exposure models are developed and used to back-calculate the maximum allowable release rates of contaminants to assure that exposures are below an acceptable safe dose. Uncertainties about key processes and parameters are treated quantitatively using probabilistic techniques and are propagated through the models. The result is a quantification of the tradeoff between the predicted emissions and the probability that the emission will exceed "safe" exposure levels given the uncertainties involved.

The methodology is applied using realistic data for a hypothetical MSWI for arsenic, beryllium, cadmium, chromium, nickel, mercury, and dioxin emissions. Seven generic exposure routes are examined: (1) inhalation of airborne contaminants, (2) ingestion of soil contaminated with deposited emissions, (3) ingestion of vegetables contaminated by atmospheric desposition, (4) drinking milk contaminated by cows grazing on pasture lands, (5) drinking water from a contaminated surface impoundment, (6) eating fish from a contaminated surface impoundment, and (7) drinking water from a contaminated aquifer.

The relative importance of each pathway with respect to risk contribution is determined along with the level of certainty that various emission rates will result in acceptable exporues from each pathway. The results are useful to pinpoint critical contaminants and exposure routes at any site, provide a logical and defensible basis for requiring a more detailed analysis and information, and can be used to help assure that a consistently high degree of public protection is obtained without over or under regulating any given site.

INTRODUCTION

This paper presents a quantitative risk analysis screening methodology using realistic data for a hypothetical municipal solid waste incinerator (MSWI) as a case example. The method determines acceptable emission rates based on an airborne contaminants toxicity (characterized by a yearly acceptable dose rate derived from standards, criteria, or cancer risk) and the contaminant's ability to be taken in by the population surrrounding the site (described by using exposure pathway modeling). The preliminary screening approach allows the focusing of attention on critical contaminants and exposure routes.

In order to estimate acceptable emission rates, the first task is the development of a criterion human dose rate for the chemical species of interest. The criterion dose rate, expressed in terms of mass intake per year, is the level at which it is assumed that human health is adequately protected. Without this dose rate, no acceptable emission rate can be developed.

Criterion intake rates or doses were derived for arsenic (As), beryllium (Be), cadmium (Cd), nickel (Ni), mercury (Hg), chromium (Cr), and dioxin (as 2,3,7,8-tetrachlorinated dibenzo dioxin). These substances were chosen for preliminary screening because the combination of their ability to cause adverse health effects, and their predicted emission levels indicated that these would be the major contributors to the predicted health impacts.

In order to relate criterion human dose rates to emission rates, models are developed which simulate the transport of the substance from the emission source emission to the receptor for each pathway of interest. Each pathway is modeled as a series of distinct environmental compartments with the contaminant in equilibrium between compartments. This screening analysis models seven generic exposure pathways.

The seven exposure pathways are:

1. Inhalation
2. Soil ingestion
3. Crop ingestion
4. Milk ingestion
5. Surface water ingestion
6. Fish ingestion
7. Ground water ingestion

These exposure pathways were chosen because they represent or encompass the major routes of exposure for most sites located within the United States. Obviously, not all pathways may be relevant to a particular site, and pathways other than the above seven, may be important on a site specific basis. These seven exposure routes

represent a good cross section appropriate for a generic screening analysis that can be first applied to any site.

Current methods of performing exposure model calculations typically use a best estimate, or appropriately conservation estimates, for each parameter in the calculation. This results in a single estimate of exposure or health consequence. When each parameter in the calculation is treated as having only one value, the results are limited because they provide little insight into the uncertainty in the results given the uncertainty in each calculation parameter. In 1981, Envirosphere Company implemented a program for evaluating uncertainties in risk assessment models. The method was adopted from work performed by Hoffman[1] and Rish and Mauro[2] for nuclear power plant asessment and by Morgan and his colleagues[3,4] for coal power plants. This method employs the use of probabilisitc or stochastic modelling techniques.

The application of probabilistic modeling involves developing quantitative characterizations of the uncertainties associated with key model parameters. These characterizations are either probability distributions, bounding ranges, or parametric values depending on the level of uncertainty about a parameter. Once key parameters are characterized, their uncertainties are propagated through the models using a simulation technique to produce a probability distribution representing uncertainty about the model results.

MODELING OF EXPOSURE PATHWAYS

Each of the seven exposure pathways is expressed as algebraic equations which are solved backwards to calculate the emission rate which would result in the criterion dose. A detailed description of the model equations parameters and assumptions are provided below. It should be noted that the equations shown below are presented in a form which is most useful to the understanding of the model concepts (how a dose to a person is received through each exposure pathway). For this analysis, the equations were rearranged to solve for the stack emission rates.

Inhalation

$$DC = RR \times \frac{X}{Q} \times BR \times LPF + \frac{RR \times \frac{X}{Q} \times SV \times (1-e^{-\lambda_s t})}{\lambda_s} RF \times BR \times LPF$$

where: DC = dose rate criterion

RR = release rate from stack (g/sec)

$\frac{X}{Q}$ = atmospheric dispersion factor (sec/m^3)

BR = breathing rate (m^3/yr)

LPF = lung partition factor - fraction of inhaled material transported to blood through lungs
SV = effective settling velocity (m/yr)
λ_s = removal rate constant from soil (yr^{-1})
t = time of continuous emissions (yr)
RF = soil resuspension factor (fraction of contaminant in soil which is resuspended into the air)

The above equation mathematically represents the total dose rate from the inhalation of emissions. This dose rate is the sum of the emissions suspended in the plume released from the incinerator stack and the total emissions deposited on the ground surface and resuspended back into the breathing zone. The expression in the brackets allows one to calculate the equillibrium soil surface concentration by accounting for accumulation and removal over time. Soil removal is assumed to be an exponential process.

Soil Ingestion

$$DC = \frac{RR \times \frac{X}{Q} \times SV \times (1-e^{-\lambda_s t})}{D_i \times \lambda_s \times \rho} SIR \times GPF$$

where: D_i = soil depth available for ingestion (m)
ρ = soil density (Kg/m^3)
SIR = soil ingestion rate (g/yr)
GPF = gut partition factor - fraction of ingested material transported to blood through the gut

As particles from the MSWI plume are deposited on the ground, they tend to accumulate. Some are removed through weathering and degradation but some remain and accumlate on the ground over time. The amount that accumulates is chemical-depedent. The contaminated soil is available for direct ingestion which is highest in young children. For carcinogens, the ingestion rate can be normalized over a 70-year lifetime. The term in the brackets represents the resulting soil concentration (in the zone available for ingestion) and accounts for buildup and exponential removal over time.

Crop Ingestion

$$DC = RR \times \frac{X}{Q} \times SV \frac{r\,(1-e^{-\lambda_w te})}{\gamma \times \lambda_w} + \frac{CR\,(1-e^{-\lambda_s t})}{\rho \times \lambda_s \times D_R} CIR \times GPF$$

where: r = faction of deposited material on crops
λ_w = removal rate constant from vegetation due to weathering (yr^{-1})

te = growing season (yr)
γ = crop productivity (Kg/m^2)
CR = concentration ratio from soil to plants (g/Kg plant/g/Kg soil)
ρ = soil density (g/m^3)
D_R = depth of soil root zone (m)
CIR = crop ingestion rate (Kg/yr)

This equation models the contaminations of crops by the direct deposition of substances from the plume as well as uptake from contaminated soil. It takes into account both the weathering of deposited substances from plant surfaces and the removal of substances from the soil root zone. When these crops are eaten, the contaminants are transferred to humans.

Milk Ingestion

$$DC = RR \times \frac{X}{Q} \times SV \; \frac{r\,(1-e^{-\lambda_w te})}{\gamma \times \lambda_w} + \frac{CR\,(1-e^{-\lambda_s t})}{\rho \times \lambda_s \times D_R} \; FIR \times F_m \times MIR \times GPF$$

where: FIR = cow forage ingestion rate (Kg/yr)
F_m = transfer coefficient of contaminant from forage to milk (yr/l)
MIR = milk ingestion rate (l/yr)

Cows fed on contaminated crops will absorb some contaminants into the bloodstream. Once in the bloodstream, contaminants would be transferred to the milk which is subsequently ingested by humans.

Surface Water Ingestion

$$DC = \frac{RR \times \frac{X}{Q} \times SV \times A(1-e^{-\lambda_f t})}{V \times \lambda_f} \; WIR \times SED \times GPF$$

where: A = area of water body (m^2)
V = volume of water body (l)
λ_f = removal rate constant due to outfall and usage (yr^{-1})
WIR = water ingestion rate (l/yr)
SED = sedimentation factor

The equation models the deposition of a contaminant onto the surface of a lake or a surface impoundment used as a source of drinking water. The resulting concentration of the contaminant in water is

dependent on the area of deposition, the volume of water, removal by outfall and usage, and on the partitioning of contaminants between water and sediments. The area of deposition can be the same as thesurface area of the water body or can be expanded to include the whole drainage basin of the impoundment, thereby, accounting for contaminants that are not directly deposited on the reservoir, but are carried in by surface water runoff from the drainage basin.

Fish Ingestion

$$DC = \frac{RR \times \frac{X}{Q} \times SV \times A(1-e^{-\lambda_f t})}{V \times \lambda_f} SED \times BCF \times F_1IR \times GPF$$

where: BCF = bioconcentration factor from water to fish (g/Kg fish/g/l water)

F_1IR = fish ingestion rate (Kg/yr)

Fish in a contaminated surface impoundments can accumulate contaminants from the water, the sediment, or from other contaminated biota further down the food chain. If fish are consumed, contaminants are then transferred to the individual.

This model uses the same equation for calculating water concentrations as in the surface water pathway, and it further applies a bioconcentration factor to derive the concentrations of contaminants that were accumulated by fish from water.

Ground Water Ingestion

$$DC = \frac{RR \times \frac{X}{Q} \times SV \times DF}{RAIN \times K_d \times \rho \times PF} WIR \times GPF$$

where: DF = ground water dilution faction

RAIN = annual rainfall rate (liters/m^2 x yr)

K_d = soil to water equilibrium distribution coefficient (l/Kg)

PF = fraction of rainfall which enters soil

Airborne contaminants which accumulate on the ground after deposition may be transported to an underlying aquifer by rainwater leaching through the soil. The concentration of the contaminant in this leachate is dependent, in part, on its relative affinity to water. The leachate in the aquifer can be diluted, dispersed, or degraded depending on the properties of the aquifer and the contaminant. Any individual using this contaminated ground water as drinking water would therefore be placed at some risk.

Of special interest is the DF term in the model. Depending upon knowledge about site specific geohydrological characteristics, the output from sophisticated ground water transport and dispersion models can be used as values for DF, or when nothing is known about the site, this factor can be conservatively assumed to be unity.

QUANTIFYING UNCERTAINTIES

Many of the inputs used in these equations are uncertain. Some have possible values spanning several orders of magnitude. Since this uncertainty can significantly affect the value of the calculated acceptable release rates, this analysis uses error propagation techniques to establish error limits on the release rates. There are several techniques available to propagate errors. They include bounding analysis, methods of moments, and stochastic modeling.

A bounding analysis typically is used to establish upper and lower bounds on a best estimate. It requires three analyses using the median, upper, and lower bounds for each uncertain parameter. While this technique establishes limits on the best estimate, it is impossible to determine the probability of these limits. For a distribution with tails, these bounds may be as much as an order of magnitude or more outside the 95 percent confidence interval.

The method of moments analysis is an improvement over the bounding analysis since it propagates the mean and the standard deviation of the imputs through the model to calculate the mean and the standard deviation of the calculated release rate. This requires, however, that the distributions be of the same type (e.g., normal). It also limits the type of distributions that can be used to standard statistical distributions by eliminating the use of subjective and uniform distributions. Additionally, the calculations required to propagate standard deviations may become rather complex and tedious.

Stochastic modeling, which includes such techniques as Monte Carlo stimulation or Latin Hypercube Sampling (LHS), can be used to propagate uncertainty through a model to obtain a probability distribution of the release rates. This analysis uses LHS which is an improvement over the Monte Carlo simululation since it converges on the estimated distribution more quickly through forced sampling of the tails of the input distributions. This same technique is currently employed to examine the uncertainty associated with the modeling of radionuclide transport in a high level waste repository. The properties of LHS are addressed in detail by McKay, Conover, and Beckman [5] and Iman, Helton, and Cambell.[6]

The decision as to which model parameters to treat as uncertain was based upon a detailed review of the models. Parameters were selected which had uncertainties spanning a range over which the results

appeared to be significantly sensitive. There may be other parameters, which were not treated as uncertainties, which other analysts would treat as such. However, for the first order screening, the more important uncertainties have been addressed.

It is important to note that this approach will not produce a complete characterization of the uncertainty in estimating the potential health risks associated with MSWI emissions. There are still significant structural uncertainties to be considered. These are other uncertainties about the assumptions and relationships used in the models (e.g., the surface water and fish ingestion pathways would apply to lakes and reservoirs situations and not to rivers and streams).

In order to properly analyze the uncertainties involved in the estimation of health impact of emissions from MSWI facilities, it is necessary to have a comprehensive understanding of the strengths and limitations of the models employed.

RESULTS AND DISCUSSION

Figures 1 through 7 present the results of the analysis for each of the seven substances. The figures depict the release rate which results in the dose criterion for each exposure pathway. These release rates are represented by the median and the 90 percent confidence interval. This interval shows the range of release rates which is between the 5 and 95 percent probability of occurrence when accounting for parameter uncertainty.

Several general observations can be made about the calculated release rates for the different substances. The criterion release rates for Be are larger than that for any of the others. This is probably due to the fact that Be is the least potent carcinogen of the rest, and it is relatively mobile in the environment. This is indicated by its extremely low gut partitioning, plant uptake factor, and bioaccumulation. Combine this with the low emission rate predicted for the hypothetical MSWI facility as well as the conservative nature of the exposure models, and one could eliminate any concern for the potential chronic health impact of Be emissions from the facility. In contrast, dioxins have the lowest calculated criterion release rates because of their assumed extreme cancer potency and their high bioavailability (high bodily intake and bioaccumulation). Hg was found to have an unexpectedly similar criterion release rate to Cr and As which are many times more toxic. This is most likely due to the fact that Hg in the organic form is highly mobile in the environment and food chains.

Several more detailed observations can be made about the calculated release rates for the different exposure pathways.

Figure 1

MAXIMUM RELEASE RATES FOR ARSENIC WHICH RESULT IN AN ACCEPTABLE DOSE

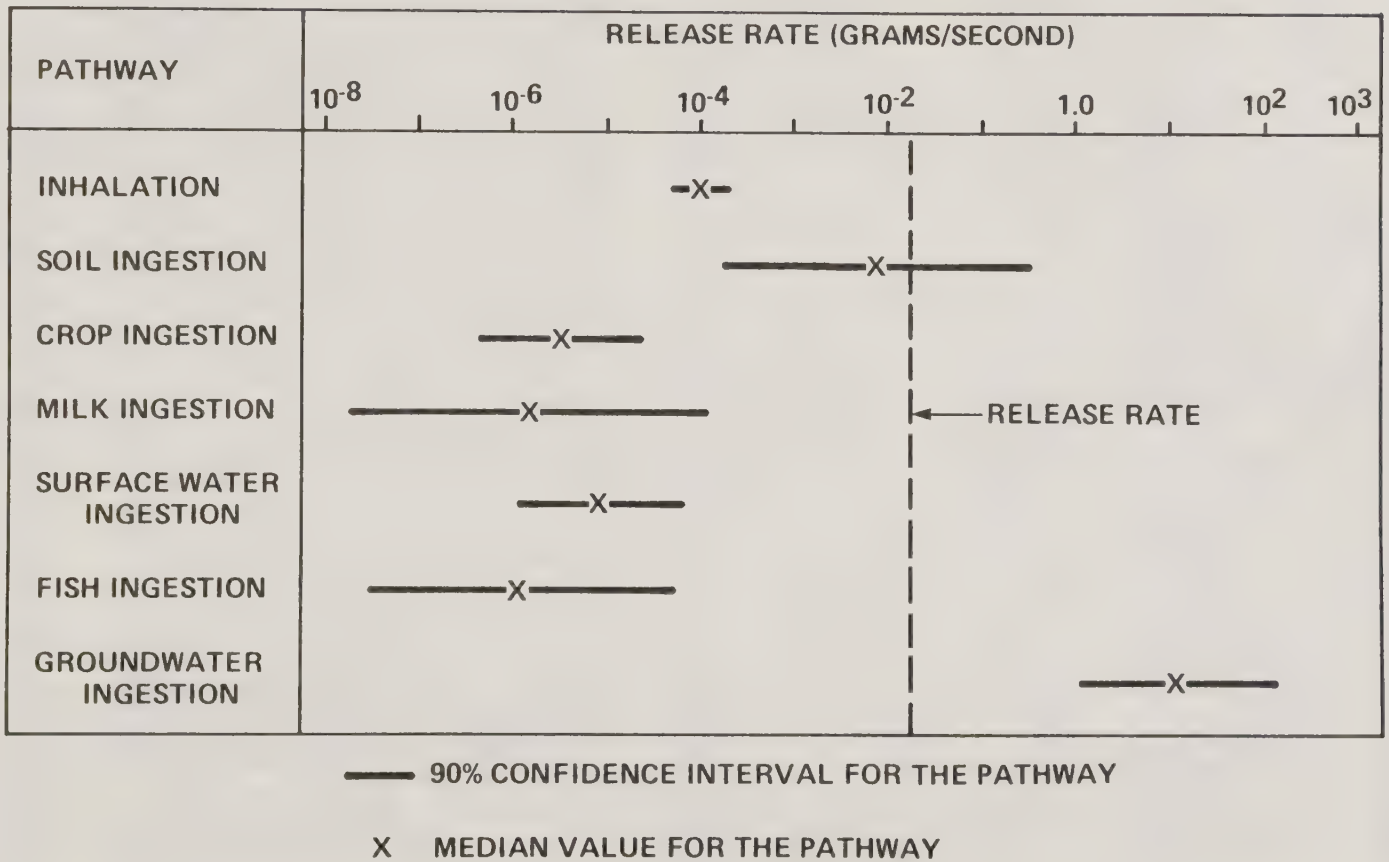


Figure 2

MAXIMUM RELEASE RATES FOR BERYLLIUM WHICH RESULT IN AN ACCEPTABLE DOSE

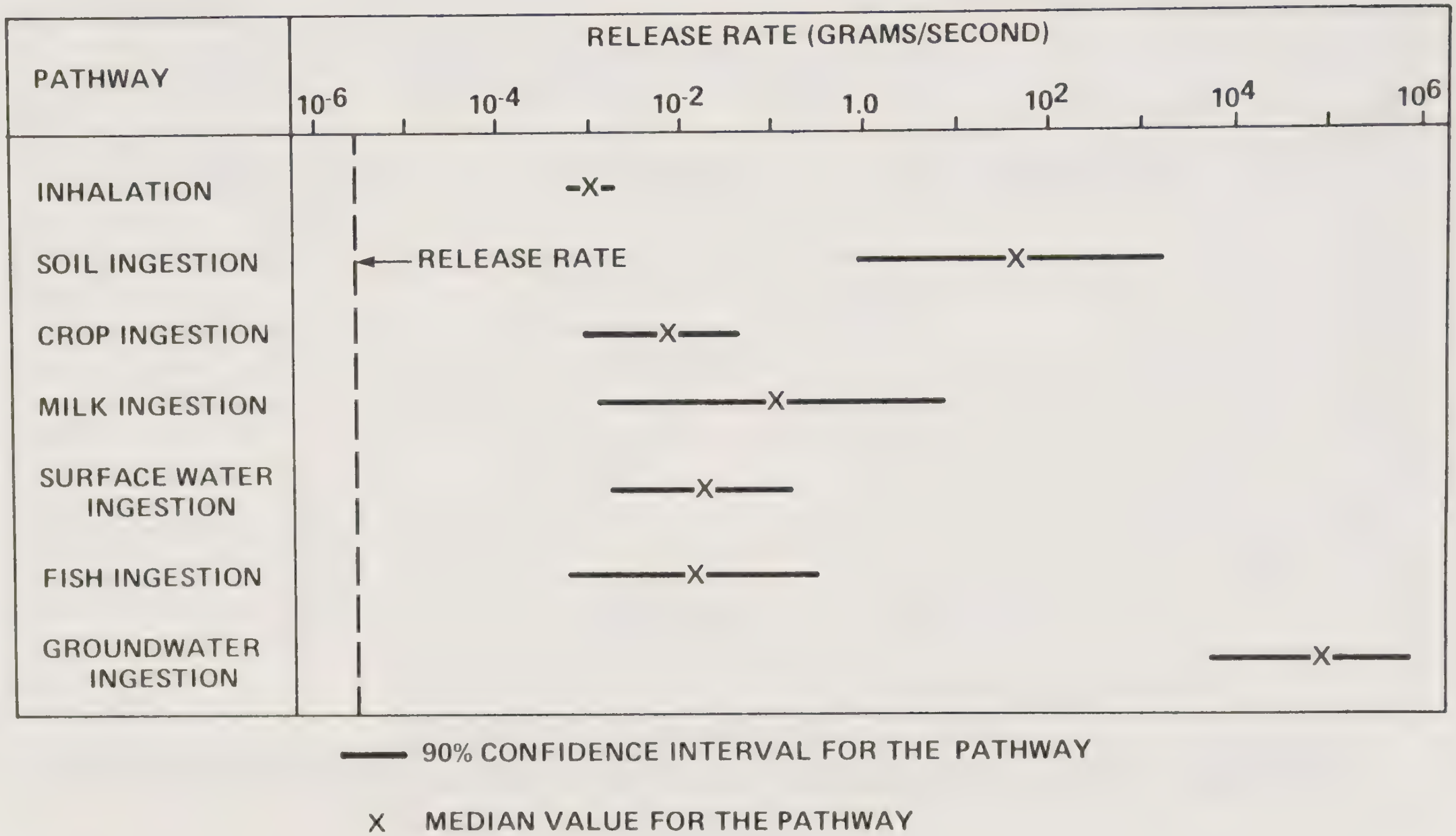


Figure 3

MAXIMUM RELEASE RATES FOR CADMIUM WHICH RESULT IN AN ACCEPTABLE DOSE

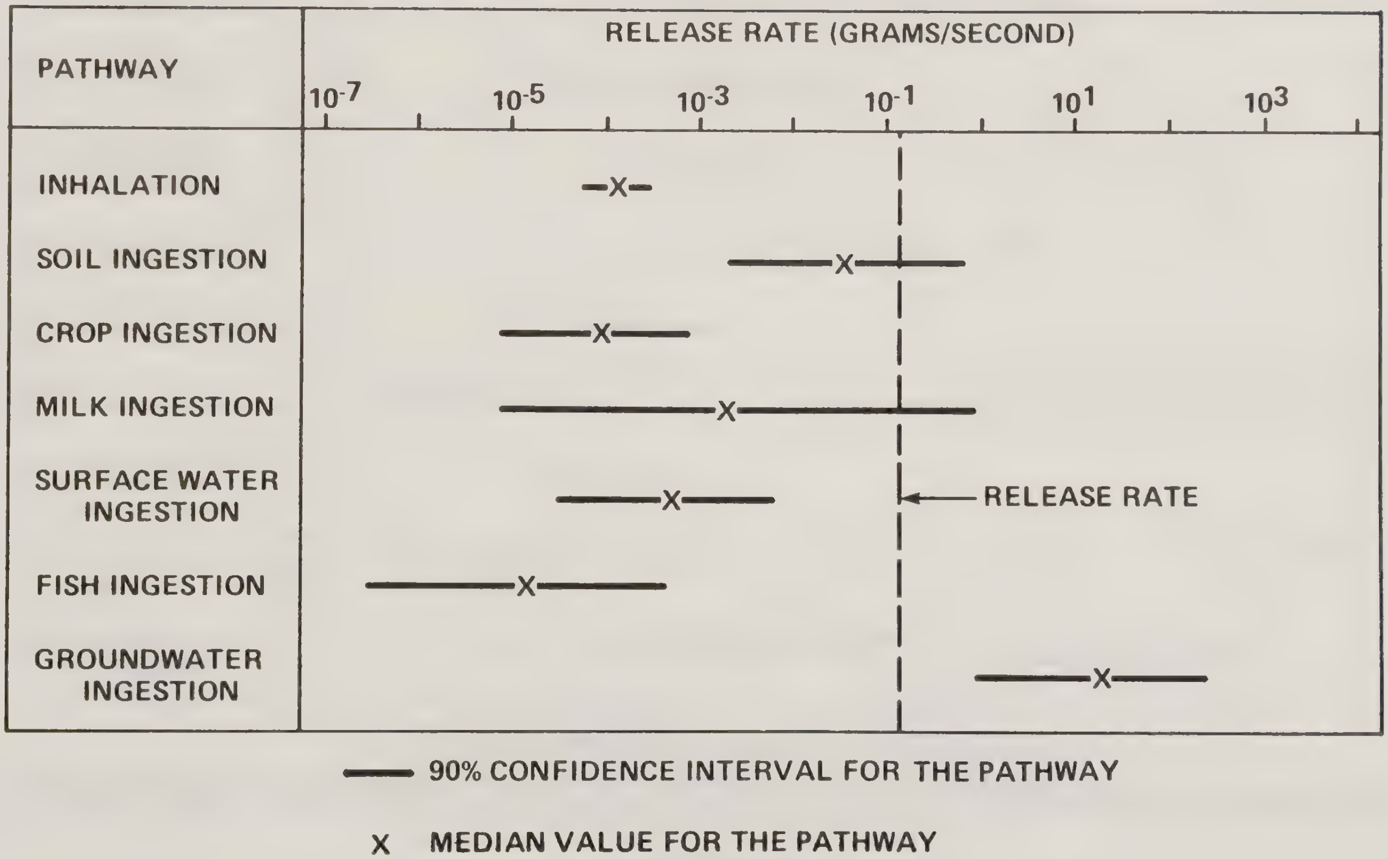


Figure 4

MAXIMUM RELEASE RATES FOR CHROMIUM WHICH RESULT IN AN ACCEPTABLE DOSE

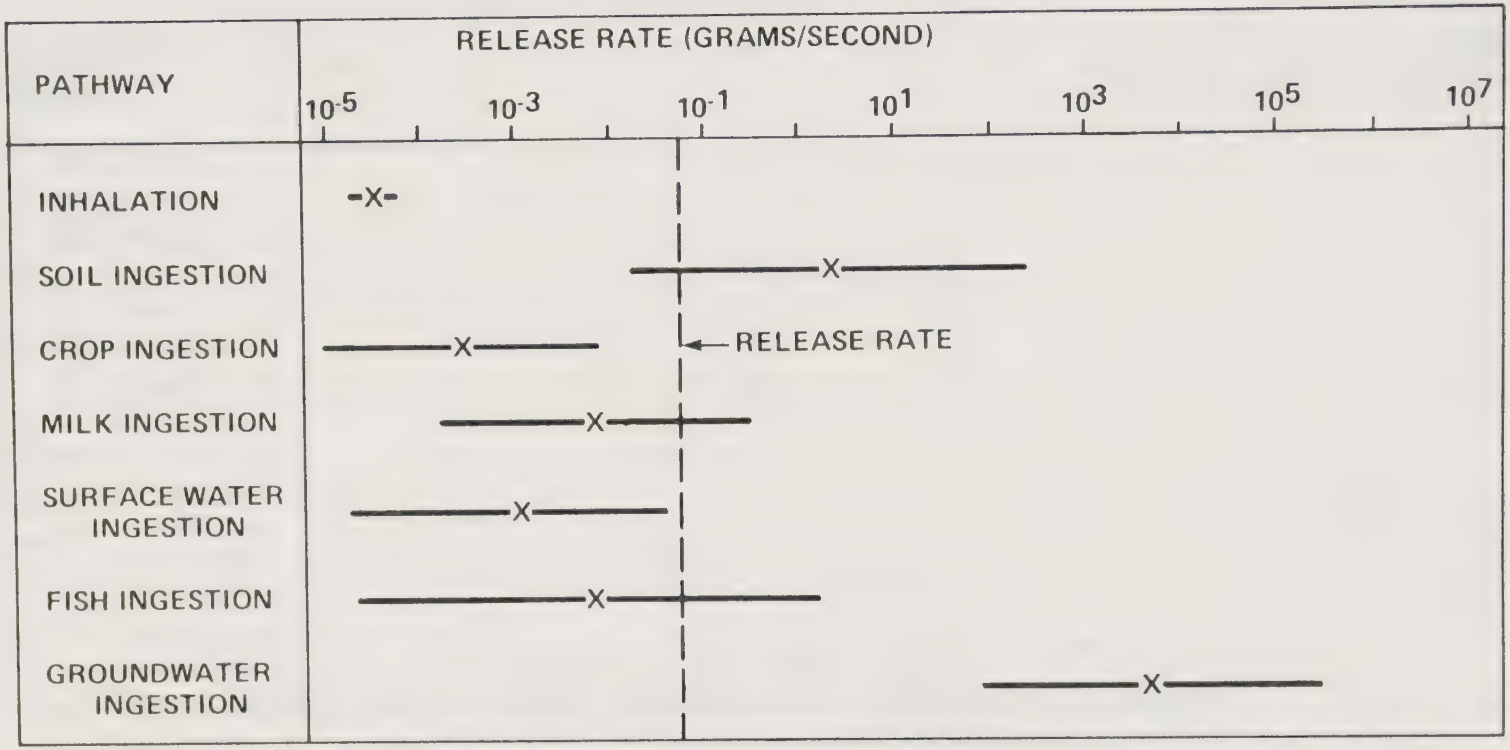


Figure 5

MAXIMUM RELEASE RATES FOR DIOXIN WHICH RESULT IN AN ACCEPTABLE DOSE

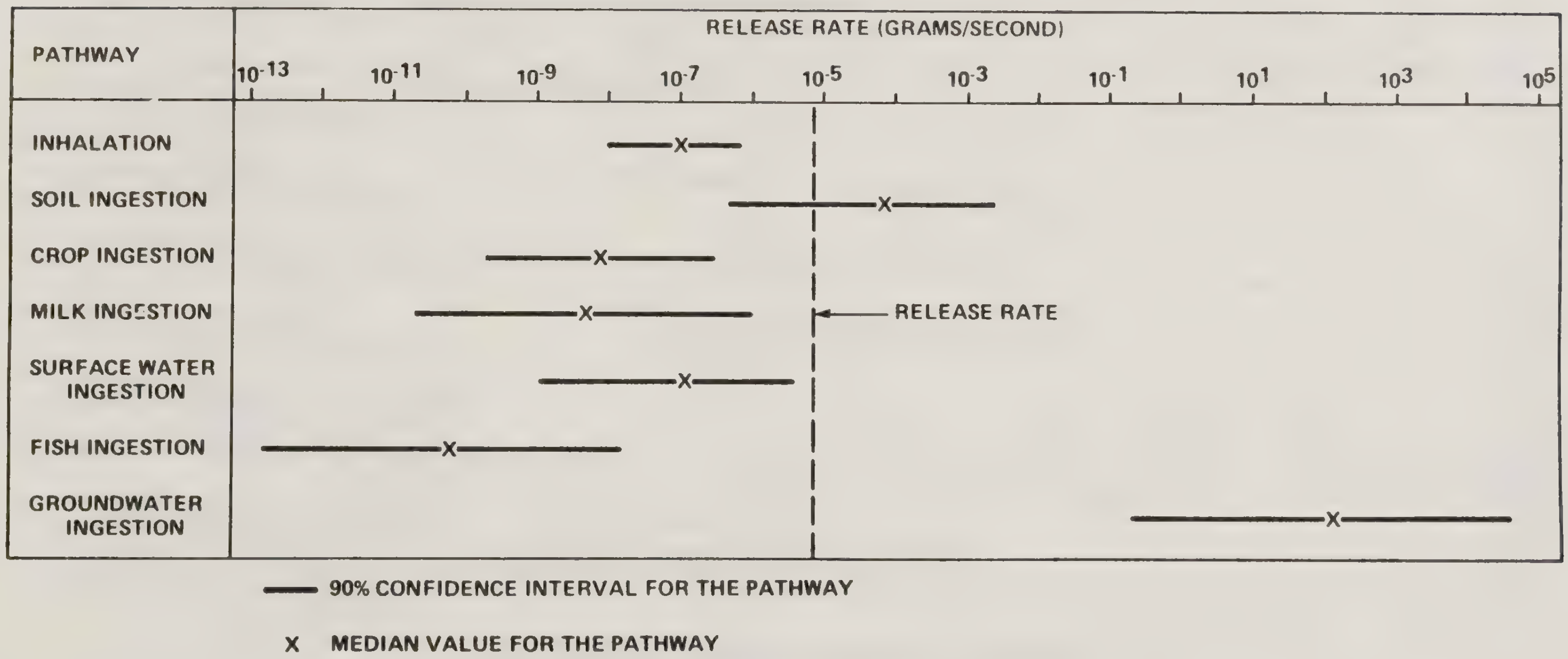


Figure 6

MAXIMUM RELEASE RATES FOR MERCURY WHICH RESULT IN AN ACCEPTABLE DOSE

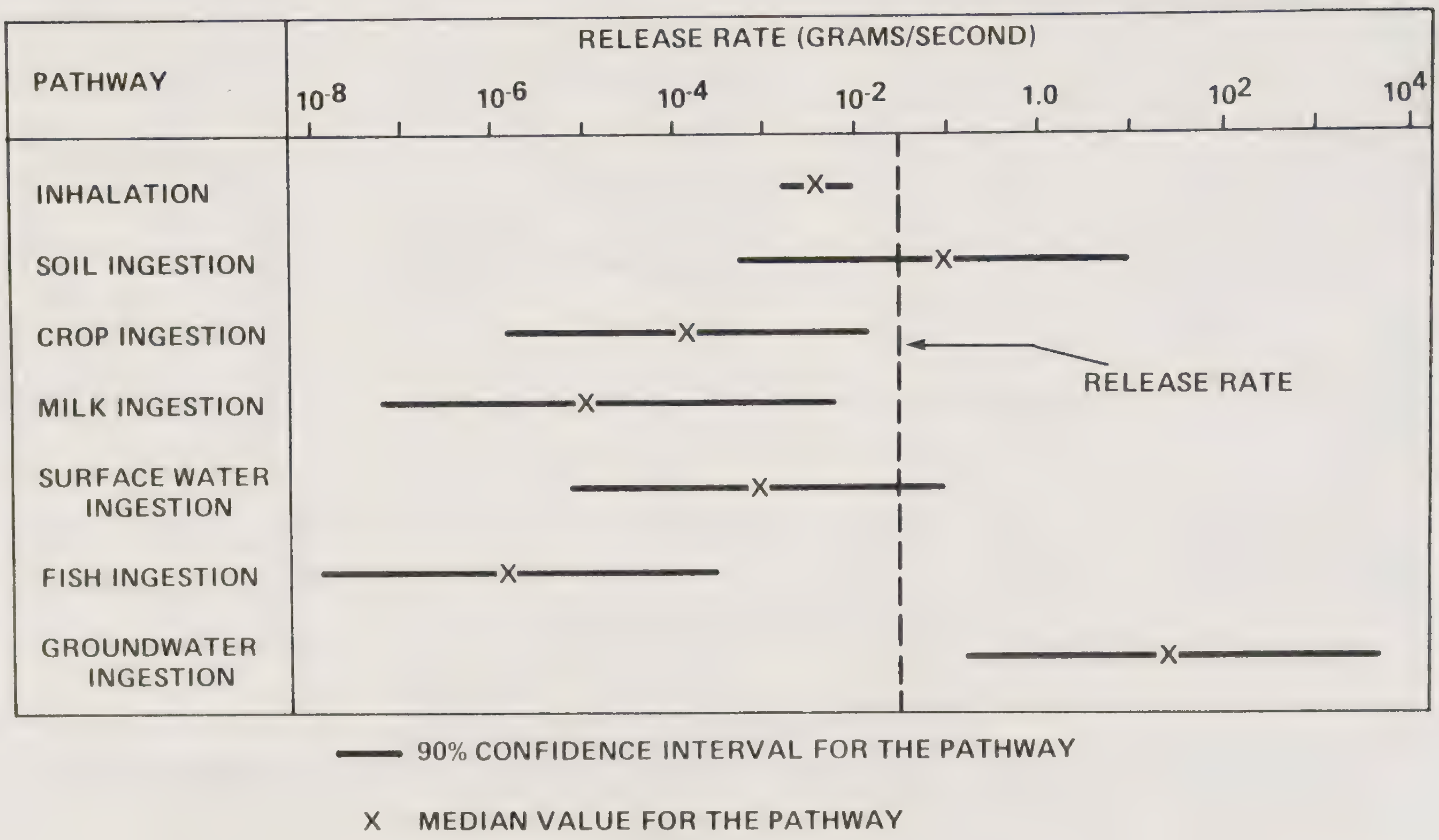
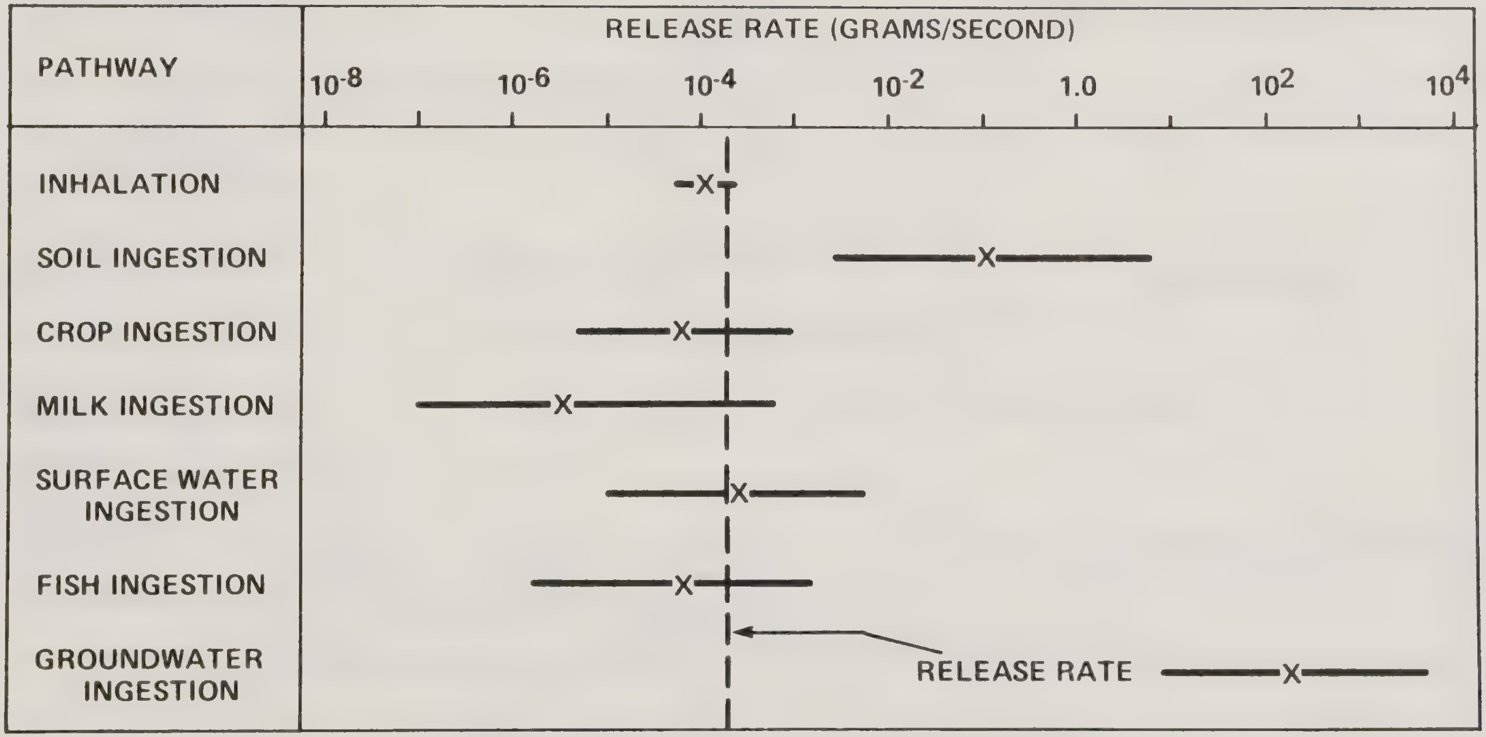


Figure 7

MAXIMUM RELEASE RATES FOR NICKEL WHICH RESULT IN AN ACCEPTABLE DOSE



— 90% CONFIDENCE INTERVAL FOR THE PATHWAY

X MEDIAN VALUE FOR THE PATHWAY

Inhalation

The results from this pathway present the least amount of uncertainity of all the pathways modeled. The 90 percent interval is less than an order of magnitude for all substances except for the inhalation of dioxin. This may be due to the large uncertainty associated in its rate of removal from the soil. In addition to Be, the inhalation of Ni is probably of little concern because the projected emissions from the hypothetical MSWI facility fall within the 90 percent confidence interval of the release rate criterion even when the model assumes that the receptor would breathe air containing Ni at the maximum annual concentration for 70 years. For all other substances, this pathway could present a significant health risk.

Before concluding the significance of this pathway for the remaining substances, a more accurate and realistic prediction of criterion release rates must be made because of the tendency of the model to over predict the potential health impacts from emission. Because the results of this model are largely dependent on the atmospheric dispersion factor (X/Q), it would be very useful to determine the annual average X/Qs for actual residences around the site. In addition, it would also be useful to know how much time people spend indoors at their homes.

Ingestion of Soils

The 90 percent confidence intervals for the criterion release rates for Be and Ni are well above those predicted for the hypothetical MSWI facility. Because of this and the fact that the ingestion model is conservative (maximum X/Q and cancer potencies), concern for the ingestion of soil contaminated Be and Ni from the MSWI should be minimal.

The results for cadmium indicate that the predicted MSWI emission is about 100 times higher than the minimum criterion emission within the 90 percent confidence interval. This result points to the idea that if cadmium is not a carcinogen, its criterion release rate would, in fact, be much higher and probably well above the predicted emission for the hypothetical MSWI thereby reducing the concern over this element by this pathway.

The same argument to a greater degree can be made for chromium whose predicted MSWI release rate is at the low end of the 90 percent confidence interval for the criterion release rate. Given the fact that the model should over predict airborne concentrations (because of the Ni of a maximum X/Q and also because Cr is probably not carcinogenic when exposure is by ingestion), little concern should be shown over danger of exposure to this element by the ingestion pathway.

Dioxins may not present a significant problem through this route of exposure either. The fact that the X/Q is probably conservative, and that this screening analysis assumes that the total dioxin emission predicted for the facility is assumed to have the same potency as

2,3,7,8-tetrachlorinated dibenzo dioxin (the most potent isomer), as well as the fact that this emission rate is less than an order of magnitude higher than the minimum criterion emission in the 90 percent interval, the concern over the potential health impacts of exposure to dioxin by soil ingestion should be reduced.

All other substances have median criterion release values that are well below the predicted site emission levels. This indicates, therefore, that site specific atmospheric dispersion factors for actual residences should be obtained by modeling.

Crop Ingestion

It is obvious from the results shown in Figure 2 that Be is not of significant concern in connection with the hypothetical MSWI facility. Ni is also probably of little concern although the figure shows the minimum criteria release rate with the 95 percent interval to be about 100 times less than predicted for the proposed facility. Since Ni is probably not carcinogenic when exposure is by ingestion (and may even be a necessary trace element) one should not be very concerned about the potential health impacts of emission of Ni as predicted for exposure through this pathway.

The results obtained for all other substances indicate that potentially significant health impacts may result from exposure through this pathway. Because the model over predicts impact by assuming maximum air concentrations, deposition, crop productivity, crop usage, and dose response, it would be very useful to obtain the following information to better predict impacts:

- types and quantity of crops grown in area
- location of farm fields and gardens in the area
- the atmospheric dispersion and deposition at the above locations
- the actual utilization of crops and garden vegetables
- the actual adverse health effects and dose response for the ingestion route.

Milk Ingestion

As was the case with exposure by crop ingestion, the screening model predicted criterion release rates that are below the predicted emissions for hypothetical MWSI facility for all the other substances except Be. Again this indicates that the following site specific information should be obtained to more realistically predict potential health impacts:

- location of cows in the area
- duration of grazing time
- proportion of cows' diet that is grown locally as forage

- o the atmospheric dispersion and deposition at the above locations
- o the proportion of milk in residents' diet that is produced locally
- o the actual adverse health effect and dose response information for the ingestion pathway.

Surface Water Ingestion and Fish Ingestion

Except for Be, all substances were found to have median criterion release rates well below those predicted for the incinerator for these two surface water pathways. It would be helpful to find out the exact locations of any fishing areas in order to obtain site specific dispersion and deposition factors for each location. In addition, it would be worthwhile to determine actual fishery catches for the area of concern.

Groundwater Ingestion

The predicted criterion emissions for each of the substances modeled were well above the releases rates for the hypothetical MSWI. Although a very conservative ground water model was used in the analysis, this indicates the ground water exposure would be of little concern.

General Concern About Emission Rates

The above discussion uses emission rates for a hypothetical MSWI facility. Like all predicted parameters, however, these values are uncertain. In view of the lack of empirical data on MSWI emissions, the uncertainty in the release rates can be large. An effort should be made in all analyses to determine the adequacy of the predicted emissions.

Individual Versus Population Exposures

The models used in this screening analysis are very conservative and have employed parameter that simulated maximum exposures of the individual to all pollutants of concern. In order to predict the actual population exposures for a particular site, population weighted atmospheric dispersion should be employed in addition to average usage and exposure model parameters. This would allow for a more realistic prediction of potential impact on the exposed population by taking into consideration the actual location of population centers as well as the average biological and sociological makeup of the residents in the area.

SUMMARY

The chronic health impacts of As, Be, Cd, Cr, Hg, Ni, and dioxins were predicted for a hypothetical MSWI facility by a screening analysis. This analysis indicates the following:

- o The potential chronic health impact of exposure to Be is not of significant concern and,
- o The potential ground water exposure pathway is not of significant concern.

From the details of this analysis the following general recommendations are made:

- o Site specific meteorolgical data and site specific receptor locations are needed to predict atmospheric and ground level concentrations of contaminants in the emissions from the proposed incinerator.
- o Specific land use demographic and agricultural statistics are needed to realistically predict the potential health impacts from potential exposure to emissions from the proposed facility.

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SOLVING THE SMALL GENERATOR PROBLEM

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SMALL GENERATORS IN PERSPECTIVE

Until recently, state and federal hazardous waste regulations have concentrated on larger volume commercial and institutional generators of hazardous waste. As a result, small generators and household generators of hazardous waste have been virtually ignored.

Small quantity generators typically dispose of hazardous wastes ranging from cleaners and paints to pesticides, automotive products and solvents, among others. Most regulators believe that small generators are the principal source of illegal dumping of hazardous wastes. If hazardous wastes are thrown away in the trash or dumped down drains, these substances can injure the refuse workers handling them, harm the water and sewage systems responsible for treating and decomposing them or pollute the surface and groundwater sources they come in contact with.

The California Hazardous Waste Management Council estimates that about five percent of the state's 10 million tons/year of hazardous wastes are disposed of illegally -down drains, dumped on land, or place in municipal waste to ultimately reach non-hazardous waste landfills. This is 500,000 tons of hazardous waste which is being disposed of improperly and unsafely.

PROBLEMS CREATED BY SMALL GENERATORS

Small generators produce wastes that contain an endless array of chemicals of varying or unreported toxicity. Although the federal Toxics Substances Control Act of 1976 established a procedure for testing new chemicals proposed for use in commercial products, it also provided a blanket exemption for hundreds of thousands of other chemicals already on the market. Some of these chemicals were never tested for product safety and may be mutagenic or carcinogenic. When disposed of in landfills or in sewage and water treatment systems, these chemicals may cause acute or

chronic health effects in people or wildlife exposed to them.

Due to their toxic nature, illegally dumped wastes pose a particular risk to the environment and public health. The risks include:

- Water and sewage treatment plants may be ill equipped to handle hazardous wastes and may pass them untreated into connecting waterways. Sewer and septic tank treatment systems can be biologically "upset" by the introduction of significant quantities of hazardous materials. The living organisms vital to the treatment process can be killed, sending toxic pollutants to sewage outlets.

- Groundwater systems and other water supplies may be contaminated by leachate from hazardous wastes moving from land disposal sites, municipal landfills, or septic tank systems.

- Firefighters are exposed to hazardous wastes when fighting fires in small businesses containing hazardous materials.

- Hazardous wastes can injure the trash collectors handling these wastes.

SOLUTIONS TO THE SMALL GENERATORS' DILEMMA

In order to reduce the hazards posed by these wastes, many cities and counties in California have developed household hazardous waste management programs. These programs have been very successful in bringing government agencies together with industry and citizen groups to plan new strategies for collecting and disposing of household hazardous waste.

The problem of household hazardous waste has also been recognized by Assemblywoman Sally Tanner, Chairwoman of the Assembly Environmental Safety and Toxic Materials Committee. She introduced AB 1809, which would mandate that:

- all County Solid Waste Management Plans (required of every county in the state) include plans to handle the household hazardous waste stream;

- all counties or local governments with a household hazardous waste plan provide public information and education material to the public;

- all hazardous household products be labelled with instructions of how to dispose of the product properly.

Due to opposition from both industry representatives and the California Waste Management Board, the bill was withdrawn from the 1985 legislative session. However, negotiations are currently in progress and a revised bill may pass this year.

However, the plight of small industrial and commercial generators has received little attention. Typically, they have been forced to fit the same system as large generators when economies of scale and competitive marketplace economics cause many small generators to resort to illegal dumping.

One study of small generator solutions was funded by EPA and the California Water Resources Control Board. The study was completed by SCS Engineers in May, 1985 and resulted in publication by the Southern California Association of Governments (SCAG) of a comprehensive pilot study for hazardous waste management of small-quantity generators (SQGs) for use in the North Hollywood area.

Though much of the data is site-specific, the study's approach, analysis and plan offers some ideas for developing solutions to small generator problems elsewhere.

Throughout the 100 square mile region near the study area, it was estimated that there was 200,000 gallons of illegal hazardous waste disposal. Put another way, that means that every acre of land averaged 3 gallons of hazardous waste being illegally dumped on it.

To stop this rampant illegal dumping, the study developed a small generator plan. There are three basic components to the plan:

1) an informational program for small-quantity generators,
2) an hazardous waste collection system, and
3) an accumulation/transfer facility (ATF) located near or in the service area.

The plan is implemented in two phases. Phase I includes the informational program and collection of the waste from the small-quantity generator followed by transportation of the waste directly to treatment, recovery or disposal facilities. Phase II continues the information program but the waste is first accumulated and stored at the centrally located accumulation/transfer facility before it is transported for ultimate disposal.

SERVICE AREA

The study area covered approximately 35 square miles in the east San Fernando Valley. One quarter of the area was undeveloped, while the remaining three quarters were a mixture of residential and commercial/manufacturing development. The program was based on servicing the needs of 480 small-quantity generators within the area that generated approximately 213,590 gallons of hazardous waste per year.

INFORMATIONAL PROGRAM

The primary purposes of the informational program are to:

1) Increase the small-quantity generator's awareness of hazardous waste management regulations;
2) Teach small-quantity generators regulatory compliance;
3) Increase the small-quantity generator's awareness of environmental and health effects of improper hazardous waste management practices; and, consequently,
4) Decrease improper waste handling practices.

The informational program employs three approaches to achieve its goals: 1) a monthly newsletter, 2) pamphlets and 3) a hotline.

<u>Newsletters.</u>

The newsletter is specifically tailored to small-quantity generators in the particular service area and includes information on the following topics:

1) Recent regulatory changes affecting small-quantity generators;
2) Identification and description of hazardous materials used in particular industries;
3) Information on proper storage or in-house treatment/disposal options;
4) Lists of haulers/recyclers/disposal facilities;
5) Information on waste exchange;
6) Availability of loan or grant monies for upgrading plant facilities;
7) Discussion of liabilities of noncompliance with examples of prosecuted generators;
8) General waste management and regulatory educational material;
9) Phone numbers and addresses of agencies concerned with hazardous waste management.

Pamphlets

Pamphlets are used as supplementary sources of information to discuss hazardous waste management issues that can't be adequately treated in the newsletter.

Hotlines

A special 24-hour telephone line is proposed to facilitate rapid communication between the small-quantity generator and the regulatory/enforcement community. Its purpose is to provide basic and technical information encompassing: identification of hazardous wastes, waste storage, recordkeeping and reporting requirements, disposal techniques, names of haulers and locations of recycling/disposal facilities.

The study suggests a computerized data base be used to provide access to requested information and reduce the time spent in answering questions. The following is a list of relevant data base suppliers:

1) CA SEARCH 1967 to Present (Chemical Abstracts Service)
2) CHEMICAL EXPOSURE (Chemical Effects Information Center)
3) CHEMICAL REGULATIONS & GUIDELINES SYSTEM (CRC Systems, Inc.) (This is an index to U.S. federal regulatory material relating to substance control, covering federal statutes, standards, and support documents.)
4) CHEMLAW (Bureau of National Affairs, Inc.) (This file contains the full text of federal chemical regulations regarding the manufacture, storage, use, transportation, and disposal of chemical substances.)

ACCUMULATION/TRANSFER FACILITY

According to the study, wastes will be hauled from the small-quantity generator to the accumulation/transfer facility primarily by a contracted-for collection service. Wastes from sources outside the established service area will not be accepted by the ATF unless the hauler is able to demonstrate that they meet the packaging, labeling and manifesting requirements of the facility.

Responsibility for identification of each waste type will rest with the individual small-quantity generator. A laboratory located at the ATF will be capable of performing simple tests on the wastes such as pH, flammability and chloride content of organic waste.

Waste drum contents will be spot-checked by the facility. If analyses show the drum contents don't comply with manifesting requirements, the facility will contact the generator to resolve the discrepancy. The facility will submit a report to the Department of Health services if there is no resolution of the problem by the SQG. Until the discrepancy is resolved, the wastes will be isolated and held at the accumulation/transfer facility.

The facility is designed to receive six types of known incompatible wastes:

1) Acidic and Neutral Aqueous Wastes
2) Caustic Aqueous Wastes
3) Petroleum Wastes
4) Recyclable Solvent Wastes
5) Non-Recyclable, Nonhalogenated Solvent and Paint Wastes
6) Non-Recyclable Halogenated Solvents

Extremely or acutely hazardous wastes will not be accepted at the facility.

Main Features of the Accumulation/Transfer Facility

1) Each type of waste will be accumulated in a separately designed compartment. Each compartment has an individual drainage sump which will be pumped out periodically and hauled to a disposal facility.

2) Each compartment will have a truck-way for direct access by the truck to the waste accumulation area with its drainage sump.

3) There will be a clean drum storage area for approximately 500 empty drums. These will be supplied to SQGs for replacement of full ones and also be used to receive the contents of leaky or damaged drums at the facility.

4) There will also be a decontamination area for cleaning of trucks and equipment with its drainage sump, and

5) An enclosed building with an office/reception room, laboratory, locker room, and equipment storage room.

Collection Containers, Quantity stored, and Length of Storage

The waste will be delivered to the facility in 30-55 gallon drums. It is assumed the drums will be 50-90% full. The drums will be designed to meet Department of Transportation and Environmental Protection Agency regulations.

Space provided at the facility for each type of waste will be either for 100 drums or for the total amount of waste that may accumulate within two months, whichever is greater.

<u>Collection and Transportation</u>

The service area is subdivided into collection areas approximately five square miles each. Each collection area will be serviced on a monthly basis by one truck that collects and hauls the individual drums to the accumulation/transfer facility. The average round trip hauling distance should range between 3 - 18 miles.

Storage drums will be collected in 14-foot van-type trucks capable of handling payloads of up to five and a half tons. The truck's walls are to be lined with a washable, nonporous surface and have logistical tracking so containers can be secured during transport.

Each collection area will be capable of being serviced in one day. The remaining working days per month will leave collection truck drivers available for emergency or unscheduled hazardous waste collection runs, drives to transfer the drums to disposal sites or performance of other ATF functions as required.

<u>Ultimate Treatment, Recovery and Disposal</u>

Hazardous wastes are ultimately transferred from the accumulation/transfer facility for treatment, recovery or disposal dependent on the type of waste and the type of hazardous waste facilities available around the service area.

SITE SELECTION

The study presumes that the accumulation/transfer facility for small-quantity generators is located in or immediately adjacent to the proposed service area. The following areas were ruled out as entirely <u>un</u>suitable sites for the ATM:

1) Areas within 1,000 ft of housing or residential zones.
2) Natural resource preserve zones.
3) Recreation and school site zones.
4) Areas within a 1,000 ft radius of a school, hospital, or extended care facility.
5) Developed public parks;
6) Areas of potentially serious geologic hazards.
7) Closed sanitary landfills (due to settlement and gas problems.)

On the other hand, the basic <u>necessary</u> site requirements for the proposed facility are:

1) It must be within or immediately adjacent to the proposed service area.
2) Preferably less than 2 acres total.
3) Minimum area of 1 acre.
4) Minimum side dimension of 150 feet.
5) Connections for basic utilities such as electricity and water should be available within a reasonable distance (i.e., the cost of developing a completely remote site would be prohibitive.)
6) Vacant land or minimal demolition required.
7) Outside of any previously screened area.

Commercial zoning, as well as residential, was determined to be incompatible for the proposed facility for the following reasons:

1) Because of the diversity of types of uses permitted in commercial zones, it is likely that the public would see an hazardous waste management facility as posing an undue threat to patrons of the various services present.

2) Traffic densities are generally higher along streets traversing commercial zones; therefore, accident rates can be expected to be significantly higher.

3) It is doubtful that the use would be permitted by local zoning authorities.

Therefore, industrial zoning areas were determined to be the most compatible with the proposed land use. For example, there is less threat of transportation accidents because traffic densities are generally lower and public concern is likely to be less if the facility is sited in an already industrialized zone.

PERMITTING REQUIREMENTS

Permits from state and local agencies must be secured prior to construction and operation of hazardous waste management facilities. The study suggests that the permitting process be expected to take at least 24 months. The principal steps include obtaining a general exemption, zoning variance, or conditional use permit from the City Planning Departments; obtaining a hazardous waste facility permit from the Department of Health Services and obtaining operating permits from the city fire, sanitation and health departments.

OWNERSHIP AND FINANCING

In terms of ownership and operation, the study suggests the most advantageous approach would be public ownership (through a local government agency) and private operation (via contract or franchise agreement.) Private operation is viewed as advantageous for several reasons:

1) Existing private firms in the waste management industry presently provide services similar to the recommended proposal. They are, consequently, experienced with the administration of a collection system and the handling of hazardous wastes.

2) Tax advantages available to private industry could be shared in part with both the small-quantity generator and the responsible government entity.

3) Open bidding for an exclusive contract by prequalified firms would ensure small-quantity generators and the government entity of reasonable prices for services rendered.

Ownership by a government entity is preferred because it is easier for it (as opposed to a private corporation) to bear the costs associated with closure trust funds and liability insurance.

In addition, governmental entities are empowered to issue general obligation bonds or revenue bonds to raise capital for construction of facilities. Interest rates on these bonds are typically low. The government also has access to general fund monies from one or more government jurisdictions which may be allotted to finance all or a portion of the facility capital costs.

CONCLUSION

Technological alternatives to the present system exist for handling household and small industrial hazardous waste generators. For household hazardous wastes, there exist a wide variety of mechanisms for funding local programs. Jurisdictions have used solid waste planning fees, solid waste enforcement fees, landfill disposal surcharges, and sewage treatment fee surcharges to fund programs. Because a funding mechanism exists, household hazardous waste programs should proliferate.

On the other hand, no reasonable financing mechanism appears to have been developed for small generator problems. Basically, a solution must be generated by either the public

or private sector. The problems that government must confront are the same that the private sector must confront-high facility costs, unreliable sources of waste, liability insurance problems, high waste characterization costs for each generator, and low volumes of each type of waste for treatment or shipment.

Generally, small generator illegal dumping is the product of ignorance and economics. While a convenient small generator transfer system and education will encourage a few companies to come into compliance, the major problems with compliance are economic. It is not clear that small generators will use an unsubsidized facility and it is clear that government is unwilling to pay the costs of a facility from general funds. In this case, we will continue to have small generators illegally dumping and government attempting to catch them.

MANAGING CHEMICAL USE, STORAGE AND DISPOSAL

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Introduction and Background

The intent of this presentation is to outline the major steps and issues which must be considered in establishing a hazardous chemical management plan for a complex and diversified organization. This paper is based primarily on experience from Stanford Universtiy, an academic and research institution. Every institution is unique in terms of its size, organizational structure and types of activities that are conducted there. As such, the recommendations made in this paper should only be used as general guidelines for formulating a hazardous chemicals management plan.

The life cycle of chemicals handled at an institution include three major components. These components are:

1) the acquisition or procurement of the chemicals;
2) their use and storage; and finally,
3) their disposal.

Any chemical management plan must therefore address the entire life-cycle of chemicals used at the institution in order to be effective.

There are five major steps to follow in setting up a hazardous chemical management plan. The first is the recognition step, in which the problems are stated and the major issues described. The second step is that of evaluation in which current "baseline" practices are documented and evaluated to accurately define the need for improvement. Once the problems and issues have been recognized, listed, and evaluated, one will then have to make recommendations for addressing them. This third "Recommendation" step will determine the shape and extent of the program. This is the most crucial phase of the process as it involves designing the actual operating plan for managing hazardous chemicals. The fourth step is the implementation and operation of the Hazardous Chemical Management Program operating plan. The fifth step, that of monitoring and certification, will ensure that the program is implemented correctly and operating as planned.

Traditional safety programs have emphasized the need to obtain support from the top echelons of management. However, difficulties arise when management tries to implement solutions for problems that users of chemicals do not recognize exist. It is therefore crucial to emphasize the importance of the recognition step to all parties within the institution, especially to those who deal with chemicals on a hands-on basis.

Having identified their target populations (i.e. chemical users and handlers), management must then undertake the task of educating them about the relevant issues and problems and about their rights and responsibilites in hazardous chemical management issues. The process of educating and informing affected populations must be carried on through all stages of the chemical mangement program's design, implementation and operation. This will help people within the institution maintain a high level of awareness about issues and problems related to hazardous chemicals management. It will also help them to realize that their participation in devising and implementing solutions is essential to the success of the management program.

Organizational Structures

Some organizations have a strong line management system. In these cases, programs can be implemented fairly and effectively by top down directives alone. However most organizations have some fairly independent sections which resist any direction from outside. This is usually true for the research division in an organization and may be the case in other areas as well. Sometimes an organization is made up of a collection of independent groups, as in universities or research institutes; in these cases, the central line management alone, is almost sure to fail at implementing the change in behavior that safety programs require. The management program must gain the support of and and encourage participation from all levels of these semi-independent groups, that is, from the actual users of the chemicals to the local management entities.

Life Cycle of Chemicals

When approaching the management of chemicals, care must be taken to include all of the components of the life cycle of chemicals in the organization. Many of the same issues will appear in all components of the chemicals life but the methods of managing these issues will vary.

In some institutions there are many procedures for purchasing chemicals that vary within each local group. The acquisition or procurement of the chemicals usually depends on the needs of the individual users, however, procedures for purchasing should be centrally controlled.

The proper use of chemicals in labs, shops, studios and production areas actually depends on the people using them on a day to day basis. This is where the need to involve the bottom levels of the organization is the most urgent. The central safety program will establish policies and guidelines for safe practices but they must be implemented with the support of local personnel. The definition of responsibilites for safe handling of chemicals is necessary for personnel to know where to look to get this information and problems solved.

The disposal of chemicals is the system most readily operated centrally in an institution. The proper disposal of waste chemicals is so specialized that a central group should gather the wastes and process them. Once the disposal program is established, education of chemical users as to the proper methods for determining what should be disposed of by the program and for meeting disposal program requirements will be needed.

Aspects of each of these components of the chemicals life cycle are managed by central management while individual chemical users determine the rest. The amount of participation required by local personnel is related to the type of organizational structure present.

Steps for Development of Programs

Recognition of the problems involved in the use, handling and disposal of chemicals is the first step to developing a chemical management program. Chemicals are used in so many areas of an organization, research, production, maintenance, art studios etc., that a careful evaluation is necessary. This evaluation should not be too specific to any one area as other uses of chemicals will invariably be discovered.

The general concerns when using chemicals include: the exposure of workers to hazardous chemicals; proper use, storage, transportation and disposal of chemicals; and the prevention of and response to accidents, spills or releases. Specific concerns are often identified in the compliance with regulations and codes. Not complying with these codes can result in the closure of facilities by officials from regulating agencies. Some of these codes and regulations are:

Model ordinance (chemical storage permit ordinance)

Occupational Safety and Health Act (administered by CAL-OSHA)

Hazardous Waste storage permit requirements (DOHS)

Right to Know laws or hazard communication standards

Resource, Conservation and Recovery Act (RCRA)

Superfund Act (CRCLA)

Federal Insecticide, Fungicide and Rodenticide Act (FIFRA).

External controls by federal, state and local regulatory and granting agencies are unavoidable. However, good faith and a decision to move in the direction of self compliance by increasing internal control will minimize external controls. It is useful to first focus on compliance with the intent of laws/regulations while designing your safety programs, and then see what modifications are needed to satisfy the letter of the law. This process will help prevent the production of useless paperwork to comply with laws or regulations.

Insurance and liability concerns must also be taken into account. Handling hazardous materials can have a large impact on insurance premiums due to the large potential for loss due to an accident. An institution's reputation can be seriously damaged by an incident involving hazardous materials release or accident whether the institution was at fault or not. This could lead to the termination of grants and contracts in the most extreme cases. Proper facilities design is becoming increasingly important. The need for upgrading and replacing existing facilities due to incorrect use of hazardous materials is becoming more common and expensive.

Evaluation of current practices for handling chemicals is the next step. A survey should be conducted to provide baseline information on the management practices currently employed in the organization. This survey should include personal contact with workers to get accurate information along with possible recommendations. Information on the following topics should be gathered:

Procurement
- Types and volumes of chemicals purchased
- Procedures for chemical purchase
- Transportation method for chemicals
- Inventory control, and other in-house record-keeping

Storage
- Procedures for chemical storage/segregation
- Storage areas design
- Personnel training
- Inspections of chemical storage areas
- Labeling, signs, etc., for containers and storage areas

Use

Definition of responsibility for safe chemical usage
Labeling, posting signs
MSDS availability
Training in chemical hazards (right-to-know)
Procedure manuals and guidelines
Protective equipment use and availability
Emergency procedures
Safety committees and safety coordinators
Who pays for safety needs?

Disposal

Disposal practices (sink, garbage can, proper waste program, recycling, treatment, etc.)
Hazardous waste management plan
Final destination of hazardous waste
Who pays for waste disposal costs?

Also inquire with other organizations similar to yours as to what they are doing to manage their hazardous materials. There is no need for us all to reinvent the wheel every time a safety program is initiated.

When making recommendations, be sure to establish priorities. The recommendations should be realistic and pragmatic, and, they should involve several steps for implementation. We suggest that a set of tightly scheduled temporary measures be recommended to address the most urgent problems, while permanent solutions should be carefully studied and proposed for a more distant future. Pressure from concerned parties should be taken into account as well. These include federal, state and local regulatory agencies, administration, users of chemicals, and the general public, among others.

Other limitations affecting the types of recommendations possible will be due to institutional restraints, including available staff and financial support. Recommendations should include requests for the following items: top-down support for the program by administration or management; a mechanism for getting bottom-up support from chemical users; well defined responsibilites of employees, supervisors and a description of support available to implement these programs from the safety department and the administration; the establishment of a network of safety institutions programs and policies; and clearly defined procedures to solve specific safety problems and provide safety information when needed.

Since the purchase, use and waste stages of the chemical's life cycle are intimately related, a good procurement policy is mandatory to prevent problems from occurring down the line. For instance, over-ordering and poor inventory control will lead to inefficient

distribution of chemicals, storage problems, and an increase in the quantity of outdated chemicals stored in the institution. The objectives of a purchasing policy should include the following:

1) Provide accountability of volumes and types of chemicals bought by the institution.

To provide a mechanism to allow the recycling and reuse of chemicals on site,
To minimize quantities of chemicals to be stored at the facility,
To provide proper storage facilities for the chemical use areas,
To minimize the difficulty in using the procurement system so users won't circumvent the procurement system.
Flag chemicals that become hazardous or are no longer useful with age.

Recommendations for managing the use of chemicals should include an educational program to make all users of chemicals aware of the following:

Potential hazards of any chemicals they, procedures required for safe use of these chemicals, this includes the use of protective equipment (fume hood, emergency shower, eye wash, gloves, aprons, lab coats, safety glasses, face shields etc.);
The effects of inadequate purchasing practices including overstocking, overcrowding of storage space, and the high cost of disposal;
Regulations and guidelines that pertain to the use of chemicals; and
Planning work so as to use only what chemicals are necessary and to use less hazardous substitutes when possible.

To effectively implement the above programs, one needs to know the specific chemicals used in all areas of the facility, especially in research, and the amount of those materials present at any one time. Furthermore, the chemicals must be listed according to their hazards and compatible storage groups in order for the inventory to be useful. For example this information can be gathered using the Life Safety Box System (LSBS) which is an information gathering tool that allows chemical users to gather an easily accessible inventory of chemicals in a room, classify those chemicals by hazard and compatiable storage group and present that information where the chemicals are used in useful formats.

Areas in your organization that are fairly independent of line management should be made responsible for the overall obedience and adherence to the institution's safety policies. Safety committees should be formed to be the main implementing force for all of these programs. The central safety department should assist the safety

committee in this area but not try to do it for them. Many of these areas will come up with a variety of ways of implementing these programs, and this should be encouraged as it will allow the area to own the program themselves.

Once the recommendations designed above are implemented there will be an additional demand for safety information. Once triggered, this demand must be met by systems and procedures that are already in place to prevent disillusionment with the safety program.

The disposal of chemical wastes has received a tremendous amount of attention in the last six years, and it is clear that any complete hazardous materials management program must specifically address the disposal of chemical wastes. The individuals who generate the wastes must be responsible for safe storage, providing waste containers, proper identification and clear labeling of waste chemicals, a list of chemicals to be disposed of, and in-lab treatment if appropriate. The central waste program should provide waste pick up services from the generators, packaging for off site disposal or treatment, manifests for external disposal and ensure that the materials' final destination is environmentally sound. Many organizations will also want to implement some on-site treatment, recycling, or incineration of hazardous wastes where possible. In some cases, funding of this program should be provided for through general overhead monies rather than through direct charges to users. This will remove the incentive to dispose of chemicals improperly by pouring them into the sewer, dumping them into the trash or by other inappropriate means.

The implementation step takes perseverance to achieve, as any new program or change will initially meet with resistance. If the recommendations are well thought out and include enough flexibility to allow for changes as you learn through doing, they should eventually succeed. Large programs should be implemented in small discrete steps to prevent overcommitting time and resources to a large project tht may be inherently flawed.

The fifth step of monitoring and certification is similar to the second step of evaluation, only it is performed after the safety program has been implemented. This allows the quantification of the success or failure of the safety program. This program will have to be continuously cycling through the five steps to keep abreast with the changes in the system. New laws, regulations and projects will demand that your safety program change with them. Critical evaluation will allow the organization to prevent committing itself to large mistakes, and allow it to benefit from experience.

The most important step in this process is the recognition step. It is essential that personnel at all levels of an organization

recognize the need for a safety program. This recognition must also include all aspects of the chemical life cycle.

A mechanism must be designed to bring awareness of the issues involved in safe management of chemicals to all levels of an organization. We have focused at the level of the chemical user to create the demand for safety information, which leads to the recognition of safety problems. This can be achieved by using "safety information boards" and other media to alert users of their rights and responsibilites in safety issues and clearly identify the individuals responsible for providing safety information. The safety information board would be an information center located in the area that chemicals are used. Information would be posted so that it would be available to all chemical users. It would identify who is responsible for safety issues and what procedures are to get additional safety information and to solve any safety problems. Other specific information could be posted there as well.

Other media that could be used are a Health and Safety News letter, the company newspaper and the local news media. General public awareness of chemical safety has increased greatly in the last five years and will also be evident in the personnel in all organizations.

Conclusions

The development of and effective chemical management program requires that the following be considered: 1) Structure of the organization; 2) the entire life cycle of the chemicals; 3) the five steps needed to establish a program; 4) continuing reevaluation of the program; and 5) informing personnel at all levels of the organization.

The importance of creating the drive for safety programs at all levels of an organization cannot be over emphasized. This must be both in the form of management support and as participation from local personnel. Awareness of the entire life cycle of the chemicals is necessary for anyone involved in their use. Once people really want to know what the hazards are and how to protect themselves, what is needed is to have sufficient systems in place to provide that information. Methods of generating that demand include: safety information boards, news letters and other media. Methods of providing this information and meeting the safety needs of personnel include: safety committeess, the Life Safety Box System, a training program and safety professionals available to consult about specific problems. Finally, when people are participating fully in the safety program, this will naturally lead to continuous reevaluation, and updating and improving procedures as needed to respond to any changes.

ABSTRACT
MANAGING CHEMICAL USE AND STORAGE

By Jennifer Gates, Harvey Chock and Alain Decleve M.D.
December 13, 1985

This paper focuses on the management of the use and storage of chemicals in a wide variety of areas. Storage and handling practices are the responsibility of the user and hence, must be managed in a non-centralized manner. Traditional safety programs have focused on getting support from management. Difficulties arose however, when management and the safety office tried to implement solutions for problems that chemical users did not recognize exist.

Any effective management program must start with the recognition by all parties involved that a problem exists and requires solution. We have proposed to create the demand for safety information so that users of chemicals will recognize safety problems. This can be achieved by using "safety information boards" and other media to alert users of their rights and responsibilities in safety issues and clearly identify the individuals responsible for providing safety information.

The demand for information, once triggered, must be met by systems and procedures that are part of an overall hazardous materials management program. For example, the Life Safety Box System (LSBS) is an information gathering tool that allows chemical users to gather an inventory of chemicals in a room, classify those chemicals by hazard and compatible storage group and present that information where the chemicals are used. This system provides workers, safety, emergency response and maintenance personnel with information about chemicals present in a room in useful formats.

DO WE KNOW HOW TO CLEAN UP PCBs?

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ABSTRACT

Different cleanup levels have been sought when polychlorinated biphenyls (PCBs) and PCB-contaminated materials have been spilled or burned at uncontrolled hazardous waste sites in California and across the nation, when remedial actions were taken under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA). Likewise, cleanup levels have varied at PCB spill and fire sites remedied under different settlement agreements, court orders, other enforcement actions, and private party cleanups since national control of PCBs was initiated via the enactment of the Toxic Substances Control Act of 1976. Consequently, the regulated community has received mixed signals about safe levels of PCBs that may be left unmanaged at sites, and the appropriate factors to consider when remedying releases of PCBs.

However, Federal and state agencies have responded with a constantly evolving framework of regulations, policies, and guidance, usually focusing on the storage, transportation, and use of PCBs in commerce, and on disposal requirements for PCBs and PCB materials having concentrations exceeding 50 parts per million (ppm). Efforts to establish one universal set of safe exposure levels for cleanups have been hampered by controversy among environmentalists, health experts, regulators, and the regulated community. Disagreements have centered on the toxicological evidence to support cleanup levels below 50 ppm, and by federal regulations that currently allow PCB cleanup levels to be set independently by each of the U.S. Environmental Protection Agency's (EPA's) Regional offices.

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* The views presented in this document are those of the authors, and do not necessarily represent the views and policies of the United States Environmental Protection Agency or the California Department of Health Services.

New spill cleanup and disposal policies will be available within the next few months from both EPA and the California Department of Health Services. The draft federal policy has been under development since 1982. It is based on EPA studies of PCB releases, recent Agency reviews of health risks associated with various exposure levels, and a consensus proposal submitted to EPA by industry and environmental groups. The EPA policy likely will establish several levels of cleanup below 50 ppm, based on the principle that risks from PCBs (and thus, appropriate cleanup levels) vary according to the amount spilled, the location (high-contact, low-contact, or restricted-access areas), and the nature and size of the population exposed. The CERCLA program may use this principle, to the extent that it is applicable or relevant and appropriate, to help select site-specific cleanup levels.

The Department of Health Services (DHS)is preparing a policy for its Regional offices that sets levels for disposal and spill cleanups of PCBs. The policy will provide different requirements for PCB solids with levels above 50 ppm, and for liquids above 5 ppm. Its implementation will be on a site-by-site basis, using the California Site Mitigation Decision Tree with full consideration given to the draft EPA policy.

The regulatory experience with PCBs over the last 10 years suggests that no single cleanup level is likely to apply universally to all PCB release and exposure scenarios. However, forthcoming policies from EPA and DHS will provide both the regulators and the regulated community with tools to assist in selecting the appropriate remedy for PCB releases, given all the factors pertinent to the remedial design process at each site.

LOSING IT IN THE GROUND

SELECTING BOREHOLE LOCATIONS AND SAMPLES FOR ANALYSIS USING PORTABLE GAS CHROMATOGRAPHY

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INTRODUCTION

Soil samples were analyzed in the field using a portable gas chromatograph with a photoionization detector to determine borehole sample locations and depths and to choose whether a given sample should be sent to the laboratory for analysis. Use of the instrument allowed real-time determination of the areal and vertical extent of contamination during the initial visit to a new area of a previously-studies site.

The objectives of this paper are to provide an illustration of the cost-effective way in which several phases of site investigation were compressed into one phase, and to suggest other potential applications for portable gas chromatographs.

BACKGROUND

The site is in the Niagara Falls area of upstate New York adjacent to the Robert Moses hydroelectric facility on the Niagara River. The study was conducted on and adjacent to a former chemical plant which ceased operations in 1976. The plant produced carbon tetrachloride and various metal chlorides. The primary organic feedstock was carbon disulfide which was reacted with chlorine to produce carbon tetrachloride and sulfur chlorides. A pesticide intermediate, parachlorothiophenol was produced from chlorobenzene and the sulfur chlorides. In addition, methylene chloride and tetrachloroethylene had been brought into the site in bulk and repackaged. The plant site had been razed prior to the commencement of this study. There was no knowledge of disposal by landfill or injection wells at the chemical plant property. However, two inactive former land disposal areas used by the chemical plant are located immediately adjacent to the eastern portion of the former chemical plant, on property owned by the New York Power Authority.

On the site, the average depth of overburden is 16 feet. The Lockport Dolomite Formation lies below the overburden and contains multiple water-bearing zones. Ground water from the site drains into the Niagara River and from there into Lake Ontario, the fishery for the Toronto area in Canada.

In the initial phase of site investigation in 1983, 88 boreholes were emplaced and 39 monitoring wells were installed. These included upgradient wells at three locations, at which soil samples were also taken, wells and soil borings around the former disposal sites, and wells and soil borings on and down-gradient from the former chemical plant site. Thirty-nine wells were needed because of the large area covered by the study site and because two different aquifers in the uppermost rock formation, the Lockport Dolomite, were to be sampled.

The only criteria that were used in 1983 to position the drilling rigs and to decide whether the split-spoon samples collected should be analyzed were: 1) limited knowledge of former on-site operations and 2) apparent soil contamination suggested by visual field observations and judgements. The regulatory agencies required continuous soil column sampling but permitted field judgements to determine which samples would be analyzed. About 150 soil samples were sent to the laboratory from the approximately 500 split-spoons collected and opened during the drilling operations.

Since analytical results from the laboratory were not immediately available, demobilization of on-site equipment and workers occurred before it was known that volatile organic compounds (VOC) were present at several borehole locations. Thus the areal extent of contamination at these locations remained undetermined. Additional work in subsequent phases would have been required to define these contaminated areas.

For considerations outside the scope of this paper, a decision was made to shift the location of the planned hydroelectric facility. Because the planned construction excavations would now be in a slightly different location, additional on-site soil borings were planned in previously uninvestigated areas.

For the study discussed in this paper, cost and schedule constraints made it necessary to determine the extent of any soil contamination without requiring multiple mobilizations and demobilizations. Several soil gas and extraction analysis screening techniques that would allow real time determination of which samples contained contaminants were evaluated. After a review of the literature and discussions with Dr. Tom Spittler at the EPA Region 1 Laboratory, a decision was made to seek a rapid turnaround soil gas screening technique. The decision was based on minimizing sample work-up requirements and minimizing analysis turnaround time. Several soil gas screening techniques were reviewed, including: a mass spectrometry technique using the mobile TAGA made by SCIEX of Toronto; two different adsorbent burial/recovery/analysis techniques (e.g., PETREX); laboratory level gas chromatography (GC) techniques incorporated in mobile vans by Tracer Research Corporation of Tucson; collection of samples with rapid turnaround of laboratory analyses; and use of various "portable GC" units. A decision was made, on the basis of effectiveness, reliability, ease of maintenance, rapidity of result availability, and cost considerations, to use a portable GC. The unit chosen was an instrument made by Photovac Inc. of Toronto, the Photovac 10S50.

The Photovac 10S50 is a gas chromatograph with a photoionization detector. It is highly portable, measuring about 18" by 6" by 13" and weighing about 26 pounds. The unit allows software-selectable GC column arrangements which include pre-column/backflush (in which all peaks eluting after a given time are eliminated) as well as computerized peak identification and quantitation, autocalibration, printout of compounds by name with ppm concentrations, a built-in multi-color printer-plotter, and variable period time-weighted averaging. The unit has a built-in suction pump, a built-in rechargeable carrier gas reservoir, and can hold an automatic calibrant container. Individuals with modest technical background can be trained to operate the device under a variety of circumstances with 1-2 days of training provided by Photovac.

FIELD SAMPLING AND ANALYSIS PROCEDURES

The objective of using the portable GC was to determine as quickly as possible if contaminants were present at a given borehole location. Two methods were available to accomplish this. In the first a vapor sample would be collected from the borehole and injected directly into the GC. In the second method a soil sample would be collected, placed into a VOA vial, and a vapor headspace sample obtained from the vial. In either case, a gas volume between 10 ul and 3 ml would be injected into the GC using a gas-tight syringe.

It had been planned to obtain a vapor sample from the borehole using the instrument's built-in suction pump. However, since the work began in November 1985 after a period of moderate rainfall, and ambient temperatures ranged from -5 C to +10 C, it proved to be impossible to collect borehole gas without potential exposure of the GC columns to liquid water which would render them unserviceable. Thus, an immediate procedural revision was made to examine headspace gas above soil and water samples collected in VOA vials from the boreholes in the overburden.

A special tool was devised from stainless steel to remove soil from split-spoon samplers so that the sample could be inserted into a volatile organic analysis (VOA) vial rapidly and with minimal sample handling. It resembled a cork borer or a zucchini corer with a tube of slightly smaller diameter than the mouth of the VOA vial and a solid central rod which could be inserted through the top of the tube to push the soil sample into the VOA vial. Each split-spoon sampler was opened in the

usual manner and several VOA vials were immediately filled. Those vials which might have to be sent to the laboratory were filled to the maximum extent possible and placed in coolers, in contrast to the vials which were used for on-site GC analysis in which a headspace volume of several milliliters was left.

Several techniques were used to increase the concentration of contaminants in the headspace volume: use of the warm air stream emerging from the windshield defroster in a van, use of hot water, and use of an electric frying pan with sand or sand and water as a heating bath. All of these methods worked quite well. If the GC column became saturated during an analysis because a sample had high VOC concentrations, the GC was cycled automatically with carrier gas alone until the column became clean. Reanalysis of a smaller headspace gas sample could then be performed. Use of a sample which had never been heated could also be attempted.

The Photovac 10S50 was used both in the back of a van which moved around the site with the drill rigs and in an on-site trailer. While in the van, it operated from a 16-hour batter pack. (The van battery could also have been used through the cigarette lighter connection. While in the trailer, it was connected to the 110 volt power supply provided to the trailer. Both locations were satisfactory; the trailer provided a larger workspace and was easier to maintain at a constant temperature. Carrier gas was supplied from tanks of low hydrocarbon (0.1 ppm) low moisture air. A variety of calibrants were used: headspace samples from VOA vials containing a variety of neat solvents in aqueous solutions, gas samples prepared from neat solvent vapor diluted with carrier gas in a TEDLAR bag, and a certified calibrant containing all major contaminant species which was provided by Scott Environmental Technology.

During the course of taking samples, two drill rigs were operated simultaneously; while one was collecting samples, the second was undergoing decontamination. The split spoons samplers were initially cleaned with laboratory detergent in deionized water (DIW), DIW, isoprophyl alcohol, hexane, isoprophyl alcohol, and two successive DIW rinses. It was soon realized that a clean sample (i.e., clean as determined by GC analysis) implied that the sampling equipment (i.e., the split-spoon samplers) needed only minimal decontamination, and the decontamination procedure was accordingly reduced. This also eliminated

the problem caused by decontamination procedure residuals, for among the conclusions of this study is that two successive final rinses with DIW, however carefully done, do not remove residuals of isoprophyl alcohol and hexane from the prior rinse.

DECISIONS BASED ON FIELD SOIL ANALYSES

A gas sample was analyzed from the headspace of a heated vial containing a soil sample composited from several split spoons collected at a given borehole. If no VOC were found, and if there was no other reason (such as unusual visual appearance) for analysis, the entire soil sample was discarded. If VOC were found, three actions were instituted: 1) head space gas from heated soil samples from the individual split spoons were analyzed to determine the vertical contamination profile, 2) the VOC-containing soil samples were sent to the laboratory, and 3) a search procedure was begun to determine the extent of contamination.

The original grid established for soil borings had them spaced about 100 feet apart on the site. When VOC were found at a particular location, the distance to the nearest uncontaminated location in each of the four cardinal directions was halved and a new borehole was drilled and sampled. Information about the contamination profile encountered was used to estimate the required drilling depth at each additional borehole. Additional boreholes were drilled until the uncertainty as to the location of the edge of the contaminated zone was reduced to an acceptable level, based on the estimated cost of remedial action (i.e., excavation and acceptable permitted disposal of the contaminated soil). Generally, provision was made for as many as 16 boreholes surrounding any at which VOC were found. The uncertainty would thereby be reduced to about 6 feet in any cardinal direction from the central borehole. At the same time, since the individual split spoons could be checked at a given location, the top and bottom of the contaminated area could also be estimated.

Thus, the GC was used as a qualitative tool to decide whether quantitative laboratory analyses following Environmental Protection Agency (EPA) - New York State Department of Environmental Conservation (NYSDEC) accepted protocols needed to be performed. In addition, the results of each GC analysis were used to make decisions about the location of the next borehole.

CONCLUSION ABOUT SOIL ANALYSES

A comparison of the Photovac and laboratory results has led to a positive correlation between 0.8 and 0.9 for carbon tetrachloride and for chloroform; i.e., if the GC indication was that either substance was present, then the likelihood was very high that the laboratory analysis would prove positive. It is important to note that the Photovac did not miss any significant contaminated soil areas; "false positives" are more likely than "false negatives."

The amount of carbon tetrachloride in the headspace volume for one heated sample when compared to the amount of carbon tetrachloride in a split of the same sample analyzed in the laboratory suggests that about 25% of the VOC volatized into the headspace. This suggests that substantial improvements can be introduced into the headspace concentration technique which would lead to lower detection limits, and more importantly, fewer false negatives. One such technique improvement would be the injection of a material into the VOA vial which would help force the soil gas to desorb. A 1N solution of NaCl is a potential choice.

A comparison of the GC result achieved with and without heating the VOA sample vial shows that the concentration of contaminants in the headspace increased by about a factor of 4-5 when the soil sample was heated to about 50°C (about 120°F) for about 10 minutes.

CHOOSING SAMPLES FOR WATER ANALYSES

After the examination of soil borings was completed, several deep boreholes were drilled into the bedrock. As these holes were being drilled, a packer was used with a bladder pump to see whether the formation would yield water in excess of any introduced; thus, after purging, an attempt was made to collect a water sample and if one was obtained, the headspace above the heated water sample was examined to determine whether VOC were present. If so, a sample of that water was sent for laboratory analysis. If no VOC were found, the water sample was discarded and the borehole was continued, with eventual installation and development of a monitoring well. Several additional boreholes already present were also examined using two packers and the bladder pump.

These tests were all done at 20 foot intervals and whenever water containing contaminants was found, the equipment was removed and thoroughly cleaned using DIW+detergent, DIW, isoprophyl alcohol, and two

DIW rinses before re-emplacement in the borehole. Thus, the potential for cross-contamination was minimized. Decontamination solvent/residuals were not found in the water samples obtained when samplers were decontaminated using isoprophyl alcohol with subsequent DIW rinses.

ADDITIONAL USES

The Photovac 10S50 was also used to monitor VOC concentrations in the air to ensure that suitable respiratory protection was used. A pumping test was initially scheduled as part of the overall program. Although it did not take place at this time, it is useful to note that the unit would have been used to examine the VOC in the headspace above water samples of the effluent from the carbon adsorption treatment units. It would have provided a rapid real time indication of breakthrough of any of the VOC. This application was accepted by the NYSDEC.

SUMMARY

During the 1985-1986 field program the ratio of samples analyzed to samples collected reduced from the 1983 value of one out of three to the 1985-86 result of one our of nine! In addition, at the conclusion of the field work, four separate soil contamination areas had been examined and defined vertically and horizontally. The vertical uncertainties in the contamination zone were less than two feet; the horizontal uncertainties had been reduced to a few feet in each direction. The use of the Photovac 10S50 during the well-drilling activities provided useful planning information which allowed fruitful decisions to be made about the depths at which well installation should occur in boreholes which had been emplaced where multiple aquifers were present. The overall cost savings are hard to quantify exactly but the lower bound can be estimated to be at least $50,000. As one additional benefit, the Photovac can also be used to ensure that on-site personnel are suitably protected with appropriate respiratory gear.

USE OF VOLATILE ORGANIC COMPOUND RATIOS TO FIND ORIGINS AND EVOLUTION OF PLUMES

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ABSTRACT

Examination of three VOC ratios (TCE/DCE, TCE/TCA, and TCE/PCE) has proven a useful tool in discriminating between contributions of different point sources to a common plume in the geographically concentrated Silicon Valley area. The distribution of the VOC ratios was inspected in light of the mechanisms of VOC transport in groundwater: advection, dispersion, sorption and retardation, and chemical and biological transformation. The observed distribution of the three VOC ratios could not be explained with respect to the operating transport processes.

INTRODUCTION

Organic contaminants are the most common environmental contaminants nationwide, being discovered in 358 of 395 hazardous waste sites documented. A subcategory of these sites are those with volatile organic contaminants (VOCs). Before 1979, aphinated VOCs, particularly trichloroethylene (TCE) were commonly used as a cleaning solvent in the manufacturing process of the California Semiconductor Industry, which is geographically concentrated in the Santa Clara Valley area; popularized as Silicon Valley. The geographic concentration of these industries coupled with common pathways of contaminating the environment with VOCs has created a situation in which a number of different companies contribute to a common groundwater contaminant plume.

Differentiating between contributions of a given point source area to a common plume is facilitated by examination of VOC ratios. Trichloroethylene (TCE) is generally ubiquitous in the Silicon Valley area and can be used as the numerator in ratio studies. Less ubiquitous VOCs

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such as tetrachloroethylene (PCE), trans-1,2-dichloroethylene (DCE), and 1,1,1-trichloroethane (TCA) have proved useful as tracers of contamination and are used as denominators. These ratios and their behavior and distribution with respect to both lateral distance from a given source and with depth yield important insights into transport processes as well as liability issues.

In this article we review the physical, chemical, and biological processes that are thought to effect VOCs in the saturated groundwater zone. This will help to illustrate the conceptual complexities of VOC contaminant transport and distribution in the groundwater. With the stage thus set we present findings on the distribution of VOC ratios in an area in which three different point sources contribute to a common groundwater plume and discuss the implications of the VOC distribution.

REGIONAL SETTING

The study area is located in northern Silicon Valley along an area referred to as the west side alluvial apron, a gently sloping alluvial sequence between San Francisco Bay to the east and the coastal hills to the west. The alluvial sequence is composed of the distal portions of alluvial fans that interfinger with a central outwash plain. This plain was deposited by ancestral streams that drained the mountains to the south. Periodic marine invasions by ancestral San Francisco Bay modified these continental deposits producing a lagoonal or shallow inland sea sequence dominated by thick clays.

SITE-SPECIFIC HYDROGEOLOGY

The site-specific hydrogeologic environment is a microcosm of the regional geologic setting. Local heterogenities in the permeability of sediments (e.g., sand- and gravel-rich, water-bearing channel versus fine-grained overbank deposits) may locally modify the dominant flow direction; south to north by northeast. Braided channel deposits have flowed across the terrain for millions of years, some being interconnected and some found as isolated lenses. The trangressions and regressions associated with water level fluctuations in San Francisco Bay may account for some of the discontinuities seen in the deeper sand sequences in the area. The contaminated aquifers are generally a few feet in thickness and separated by clay rich aquitards. Three discrete sand zones within the first 60 feet of deposits have been examined in this case study. Numerous monitoring wells were installed into each of these three aquifers.

BEHAVIOR OF VOCs IN GROUNDWATER

The principles of VOC contaminant transport in the subsurface environment are reasonably well understood. Advection, dispersion,

sorption, and reaction (degradation) are the primary mechanisms influencing solute transport. The distribution of VOCs, however, is influenced not only by the tranport processes but by the way in which the contaminant is introduced into the environment. In the case study described here, all organic liquids are assumed to have been introduced by subsurface spills or leaks as continuous sources at or near the groundwater table. The subsurface environment in the study area is characterized by three generally discernable, continuous aquifers averaging four feet in thickness in a matrix of clay. The following discussion begins with transport processes that most strongly influence migration of VOCs in groundwater.

Advection

In coarse sand aquifers such as those in the first 60 feet of alluvial deposits in the study area, advection is the dominant transport process. Advection is the transport of a solute at a velocity equivalent to that of the groundwater flow. Groundwater velocities in this area typically are on the order of 100 to 300 feet per year. VOCs do not, however, travel at equal velocities due to differences in their retardation factors.

Dispersion

TCE and/or DCE dispersion in groundwater causes mixing with uncontaminated groundwater; hence, dispersion is a mechanism for dilution. Moreover, dispersion causes the contaminant to spread over a greater volume that would be predicted solely from an analysis of velocity vectors (Anderson, 1984). Dispersion is chiefly of importance in predicting transport away from point sources of contamination. The accelerated arrival of contaminants at an observation point is a characteristic feature of dispersion that is due to shorter travel time needed along the more permeable flow paths. Velocity variations arise partly because water along the center of a continuous pore travels faster than water near the individual grains of porous material (Gillham and Cherry, 1982). These two factors create mechanical dispersion on a microscopic scale. Dispersion is greater in the direction of flow than transverse to the flow.

Sorption and Retardation

VOCs interact with aquifer solids encountered along the flow path to varying responses. This causes adsorption, partitioning, ion exchange, and other physio-chemical processes. These phenomena result in the contaminants distribution between the aqueous and solid phases, causes diminution of aqueous phase concentrations, and retardation of the movement of the contaminant relative to groundwater flow (Mackay et al., 1985). The higher the fraction of the contaminant sorbed, the more retarded is its transport. Figure 1 illustrates the relationship in a

uniform sandy aquifer underlain by a level aquitard with a continuous source of contaminants: unretarded contaminant (a) and retarded to varying degrees (R1, R2). The unretarded contaminant, such as chloride ions, moves at the velocity of the groundwater. The retarded VOC components R1 and R2 might be TCE and PCE. Table 1 shows retardation factors for TCE, PCE, DCE, and TCA as determined by Cooper, et al. (1985).

TABLE 1

Kow VALUES FOR SELECTED VOCs

VOC	Log10 Kow
Trichloroethylene (TCE)	2.29
1,2-Trans-dichloroethylene (DCE)	1.48
1,1,1-Trichloroethane (TCA)	2.17
Tetrachloroethylene (PCE)	2.88

Source: Cooper, et al., 1985.

Chemical/Degredational Transformations

VOCs may be transformed into other VOCs by chemical and biological mechanisms. The principal classes of chemical reaction affecting VOCs in water are hydrolysis and oxidation (Roberts et al., 1982). There is also evidence suggesting that certain VOC groundwater contaminants can be biologically transformed by microorganisms attached to solid surfaces within the aquifer (McCarty, et al., 1984). Studies of biological transformations of chlorinated alkenes in microcosms simulating groundwater environments indicated that PCE and TCE undergo reductive dehalogenation to form cis- and trans-DCE, respectively.

VOC RATIO HYDROCHEMISTRY

TCE/DCE

Three general ranges of TCE/DCE ratios are discernable throughout the study area (Figure 2). In the southern portion of the site, a TCE/DCE ratio ranging from a minimum of one to a maximum of ten is associated with the contaminant source area designated B. Contamination from this source appears to be transported northeast of the source and along the A/C property border. Ratios seen along the border are probably

the result of mixing of the waters contaminated by source areas B and A. Source area A displays generally higher TCE/DCE ratios (5 - 60) than source B. Waters originating from this source generally flow towards the northeast and contaminants are attenuated in the same direction. The third distinct ratio is very high, generally being greater than 500 and reaching infinity. These high ratios are associated with the northernmost point source area (C).

TCE/TCA

Three characteristic ratios can be associated with the different point source areas (Figure 3). Downgradient of source area B lies very high TCE/TCA ratios. These ratios do not fall below 1000 and often reach infinity. To the northwest of this source area lies source area A, which displays TCE/TCA ratios of between 100 to 300. Northeast of these two southerly source areas lies an area of TCE/TCA ratios that seldom are greater than 20, and can be associated with source area C.

TCE/PCE

This ratio has proven to be the most disappointing in delineating point source areas. Both point source areas B and A display TCE/PCE ratios in excess of 200 (Figure 4). In addition, each source area can be associated with ratios of approximately 400 to 1000 immediately downgradient. Differentiating these two source areas from the third source area (C) is easily demonstrated as the TCE/PCE ratios seen in the groundwater north of source C are generally low, ranging from one to fifteen.

VOC Ratio/Depth Relationships

An interesting observation of the distribution and magnitude of the three representative ratios (TCE/DCE, TCE/TCA, and TCE/PCE) is that the contaminant plumes are attenuated as migration proceeds to the north. This phenomenon suggests that retardation and preferential contaminant partitioning of the VOCs occurs during transport. This partitioning can be observed in both lateral and vertical migration. Examination of Figure 5 reveals that as advective transport to the northwest occurs, contaminants from point source B in the south migrate to deeper aquifers, a condition common in advective/dispersive solute transport processes.

DISCUSSION OF RESULTS

In order to determine whether the observed VOC ratios are a result of transport processes versus differences in source input, we evaluated whether or not the observed distribution of VOC ratios could be explicated in light of transport processes.

The advection process, if dominant, suggests that the VOC ratios, given comparable inputs, should remain relatively uniform downgradient of their sources. Examination of Figures 2 and 3, however, indicate that this is not the case. The TCE/DCE ratio is relatively low in wells at sources A and B while the wells at source C show values approaching infinity. Both the TCE/PCE and TCE/TCA ratios, on the other hand, show a reversed trend with high ratios at A and B and low ratios at C.

Evidence of the dispersion process is shown by the apparent mixing of plumes along the A/B property boundary, best illustrated in Figures 3 and 4. The TCE/TCA and TCE/PCE ratios suggest mixing between sources at A and B and B and C, respectively. Some mixing at the border between B and C is also indicated in the TCE/DCE ratios in Figure 2. However, unique source characteristics are conserved at source C compared to sources A and B.

Sorption and retardation characteristics of the contaminants TCE, PCE, DCE, and TCA as reflected in their Kow values (see Table 1) indicate that the downgradient ratio values should decrease for TCE/DCE and TCE/TCA. The TCE/DCE ratio plot shows a downgradient decrease in ratio values with respect to sources A and B, but this trend is not maintained once source C is encountered. While the TCE/TCA plot does show a decrease, this decrease is much more extreme (order of magnitude) than is expected given the similarity of their Kow values. Retardation factors for TCE and PCE predict an increase in the TCE/PCE ratio away from sources A and B towards C. Figure 4 shows a marked decrease.

Transformation phenomena, with respect to the VOC ratios investigated in this study, should be reflected in the downgradient decrease in the TCE/DCE ratio. The decrease would be due to the degradation of TCE to the trans-isomer of DCE. If pronounced degradation were occurring at the same rate at the three sources (A, B, and C), then we would expect to see a decrease in the TCE/DCE ratio distribution between areas A and B relative to C. Observed trends indicate a marked increase in the TCE/DCE ratio occurring downgradient of sources A and B.

Examination of VOC ratios has proven a useful tool in determining unique characteristics of source areas where data on the original contamination at the source area was not available. In the case discussed here it appears that the source area at point A was relatively high in PCE, source B appears to be relatively high in DCE, while at source C the principal contaminant other than TCE was TCA. Thus, VOC ratios distributions can be used to determine the VOC makeup of the original point sources of contaminants.

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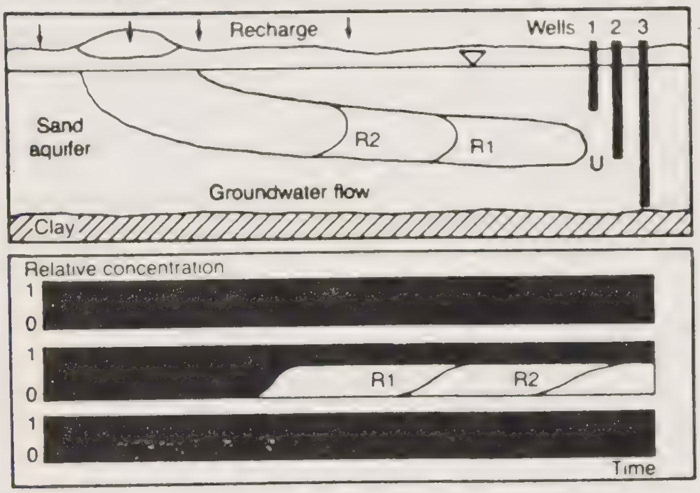
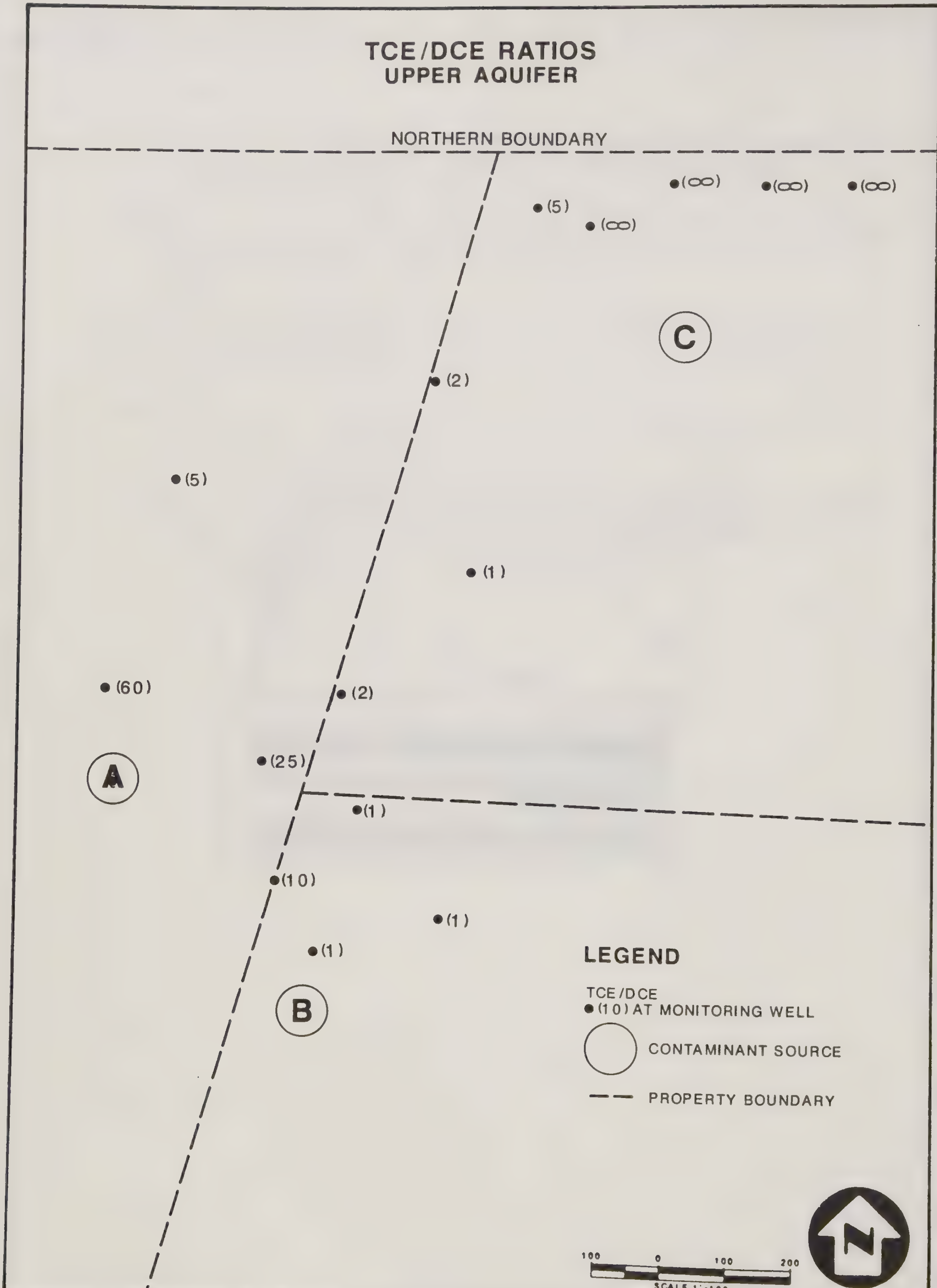
FIGURE 1

Contamination from various sources in an unconfined aquifer[a]

(a) Continuous source of three dissolved contaminants; unretarded (U) and retarded to varying degrees (R1, R2)



(Source: Mackay et al. 1985)



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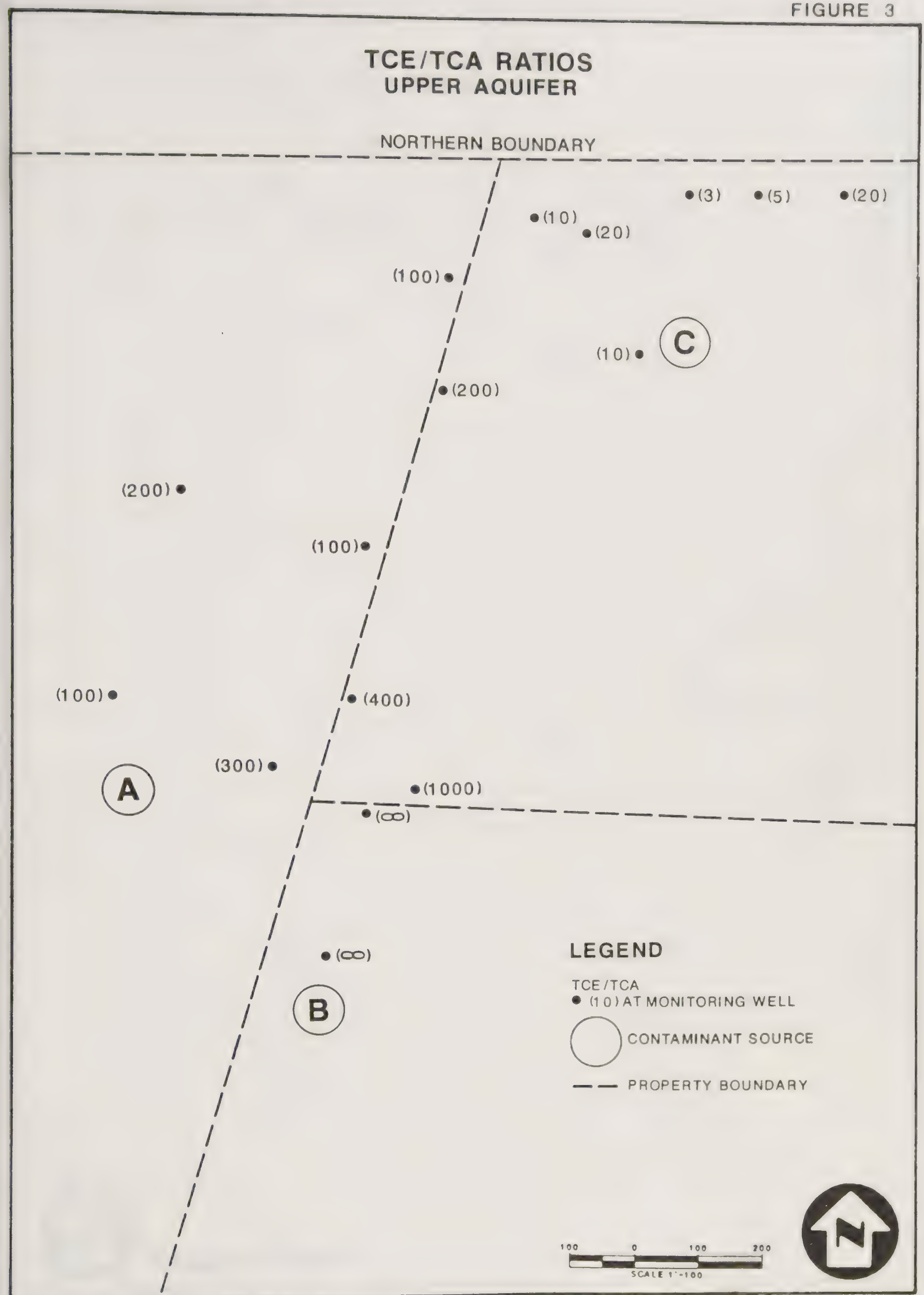

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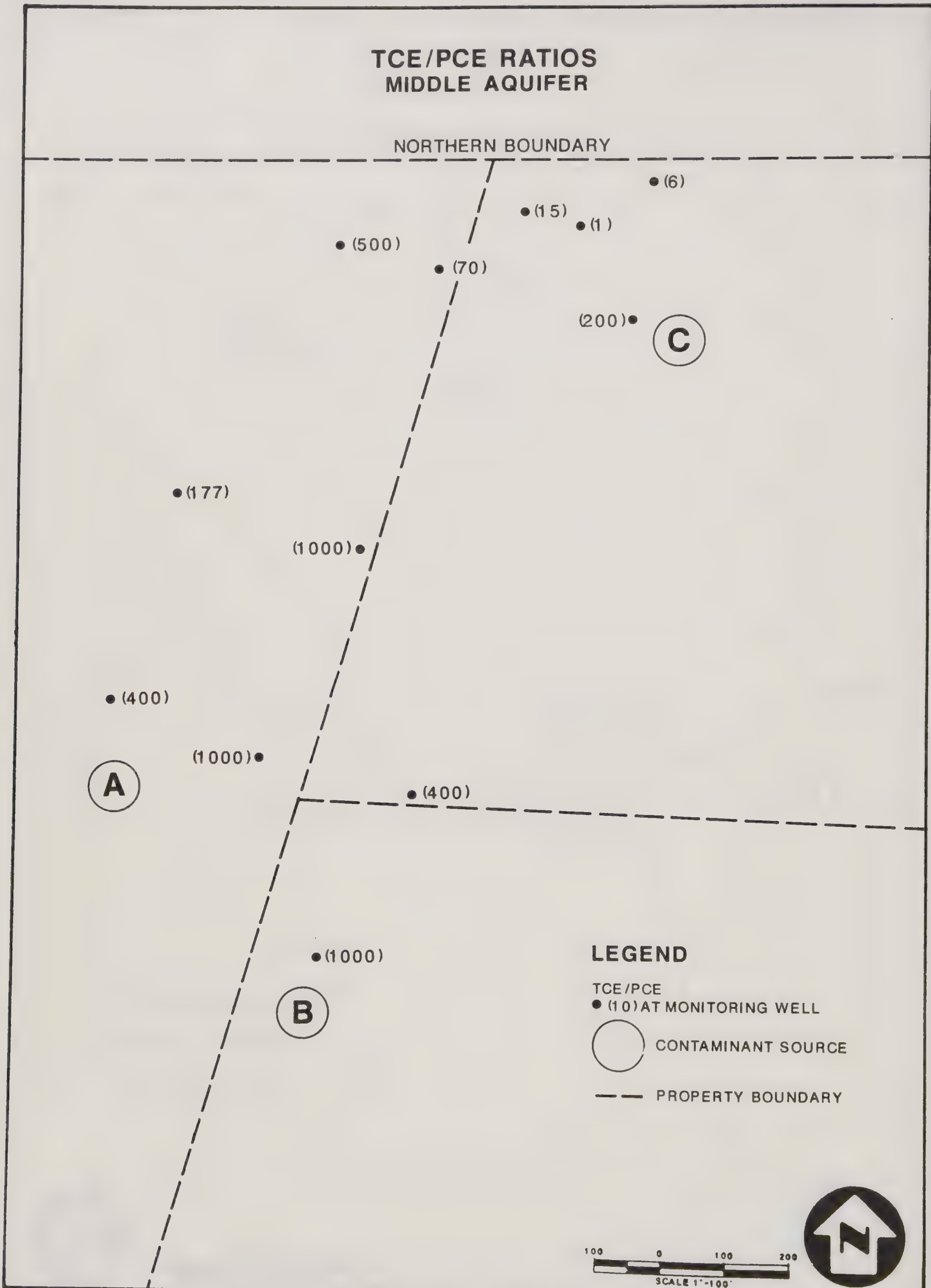

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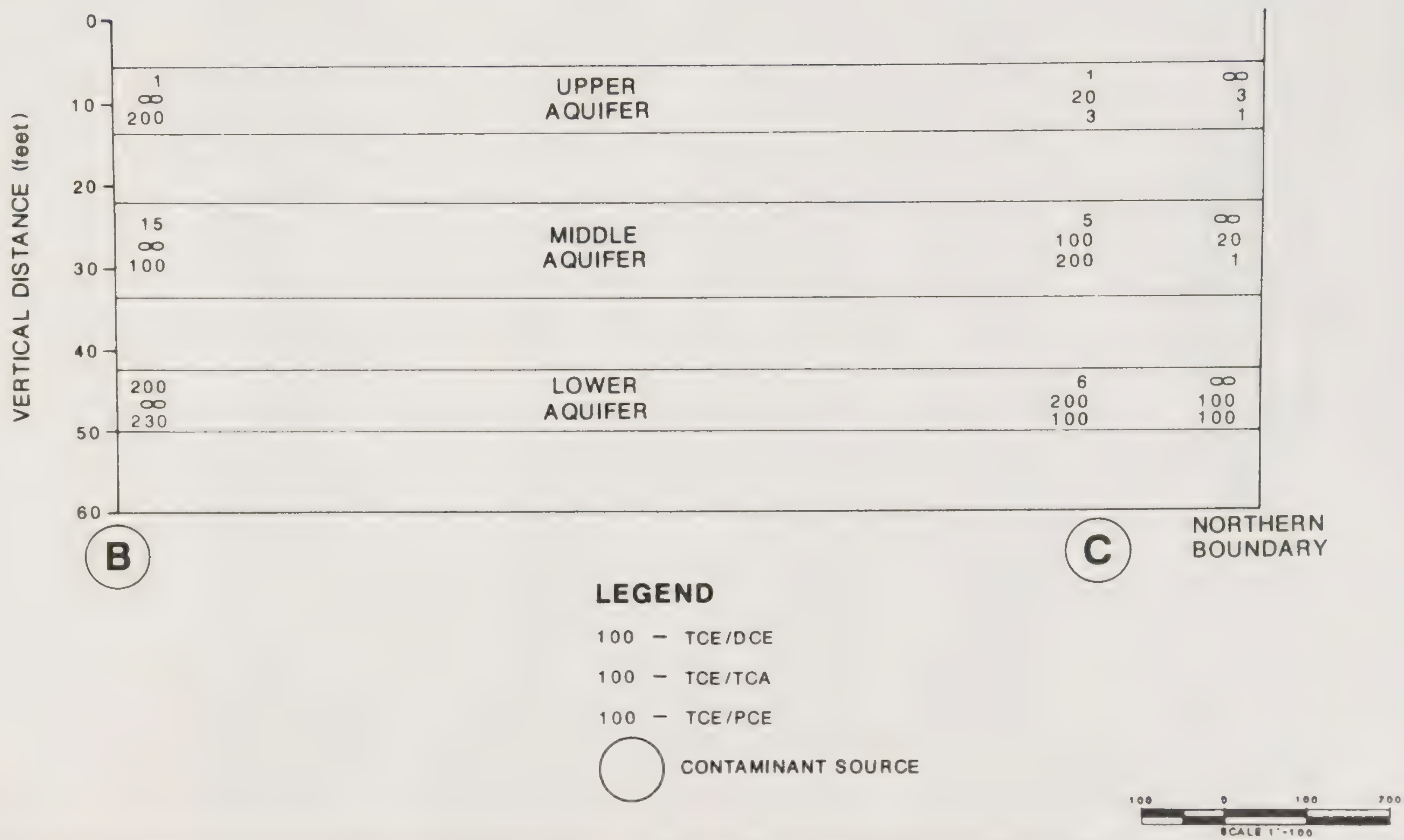
VOC RATIOS/DEPTH RELATIONSHIPS



A COST-EFFECTIVE ORGANICS DETECTION METHOD IN CONTAMINATED SOILS

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SUMMARY

A new detection method was used in conjunction with conventional sampling procedures to perform a soil contamination investigation. The site was located adjacent to a potable water reservoir. The purpose of the investigation was to determine the existence of pesticide and herbicide contamination.

The application of method, developed by Aqua Resources Incorporated and PETREX, offers an economically attractive alternative to common data collection procedures, and it can be used to guide conventional sampling, determine the extent of sub-surface organic plumes and detect and identify previously undetermined contaminants at known and suspected waste sites.

It consists in gridding the site with organics collectors and measuring and comparing relative ion flux rates.

Trace volatiles present in the soil attach on to an activated carbon collector; the mass spectra of these volatiles are computer-analyzed by multivariate statistics and used as a "signature" or fingerprint for differentiating organic sources of contamination.

INTRODUCTION

General

Static collectors have been used extensively to monitor contamination in the workplace, but until recently have not been utilized for the identification of potential contaminants in the soil or emanating from ground water. By using specifically constructed static collector combined with analyses by mass spectrometry, substances originating from contaminated soils and ground water can easily be detected just below the soil surface.

Application

Aqua Resources was confronted with a relatively large area in which suspected contamination from pesticides, herbicides and wood treatment chemicals had occurred and with the need to characterize the extent of any subsurface contamination in an accurate, timely and relatively inexpensive manner. Consideration was given to static detection systems providing a means for collection of trace quantities of subsurface derived organic contaminant. It was also desired to use an integrative technique to eliminate the short term variations associated with most gas/vapor detection methods. Previous research has shown time-integrated collection techniques yield statistically superior results when measuring flux rates compared to instantaneous collection methods. At this point, Aqua Resources considered the use of the Petrex Method originally developed to guide investigators to areas of potential oil and gas production. The method is extremely sensitive to trace hydrocarbon emission and has been used successfully to reveal the presence of oil and gas deposits by detecting the minute hydrocarbon traces leaking from such deposits.

Other advantage of the Petrex sampler for this type of study is the sampler's ability to respond to conditions within a volume of soil within some radius around and below the sampler. Thus, the sampler need not directly overlie a contamination area in order for it to respond to the contamination. This feature makes it useful for general site characterizations. In addition, under uniform geological conditions the results are at least semi-quantitative in that the amount of material adsorbed by an individual sampler will vary with the amount of contamination within its detection bulb.

This type of sampler is most useful for materials with some volatility and affinity for activated carbon. For purposes of this study the samples were analyzed for DDD, halogenated solvents, trithion, and herbicide carrier oils.

EXPERIMENTAL SECTION

Method Description

The static collector illustrated in Figure 1 was used for trapping the contaminants. It is prepared by applying predetermined sieve-sized activated charcoal to the tip (1 cm) of a ferromagnetic wire. After construction the collectors are cleaned by heating to 358°C in a high vacuum system followed by placement into a sealed culture tube under an inert atmosphere.

Once in the field, the static collectors are placed in cored holes, backfilled and left to equilibrate with soil vapors for a period of seven to thirty days. After this period the collectors are retrieved from the field and returned to the laboratory for analyses by Curie point desorption mass spectrometry.

The Curie point method allows for a clean reproducible desorption of compounds from the static trap. The compounds reported can be interpreted by mapping the relative ion count (flux) of the identified compounds. The pattern developed as a result of correlating flux data over multiple sample points (e.g., a grid) is used to determine the extent and apparent direction of migration of the contaminant plume.

Study Area Description

The area subject of this report, was approximately 60,000 square feet. The site had been used periodically to mix pesticides and herbicides with hydrocarbons for weather resist application. In addition, motorized and handheld application equipment had been cleaned at several sites in the study area and fence posts and other wood products had been treated in tanks and open pits with wood preservatives. The fact that the potential contaminations included a large fraction of hydrocarbon oils also lead to the decision to use the PETREX hydrocarbon detection method.

Data Collection

The initial soil contamination survey was conducted in early November, using two techniques. Petrex samplers, devices which collect subsurface vapor samples, were used. In addition, traditional soil core sampling was done. The details of the sampling follow.

A 43 point survey grid was established, generally concentrating in the work areas and extending down gradient. Sixty-four (64) static samplers were buried in the study area. At 21 of the survey grid sampling points, two samplers were buried; one being retrieved after seven days exposure and the other retrieved, with the remaining single sampler points, after 14 days exposure. In addition, at a site known to be free of pesticides, six additional samplers were buried as site control blanks and, at each of five suspect sites, an additional sampler was uncapped, exposed in air for approximately 30 seconds and recapped as ambient background blanks.

A soil core up to 10' long was extracted from the center of each area. Four soil cores 3' to 5' long were then collected at a radius of 5' from the center. Those four cores were spaced approximately 90° apart around the center. Four static samplers were also installed in most areas. In general, these samplers were placed at a radius of 8 feet from the center,

and spaced at 90° from each other and 45° from the short core samples. In some instances, the Petrex grid had samplers sufficiently close to the coring sites that additional ones were unnecessary. Figure 2 shows the typical sample location procedure.

The Petrex samplers were sent to the Petrex laboratory in Golden, Colorado, for analysis. All soil samples were delivered to a certified laboratory for analysis.

Analytical Methods

Table 1 summarized the compounds of primary interest to the study, α-Pinene, a material released into the soil by vegetation, was included in the list to illustrate the discriminating capability of the technique. High levels of α-pinene have been observed in other studies where significant vegetation grows.

TABLE 1. Primary Compounds of Interest

Halogenated solvents
Hydrocarbons
herbicide carrier oils
DDD
Trithion
2,4-D and related esters
α-pinene
Toluene
Phenols
Gasoline
Diesel Fuel
Creosote

Each of the 46 single samples were desorbed into a quadrupole mass spectrometer and a spectrum generated. The total flux for each sample was mapped. From this map four samples, were chosen for GC/MS analysis. The GC/MS analysis was conducted using a 30 m fused silica capillary column (J & W Scientific) on an Extranuclear GC/MS. The column was temperature programmed from 50-280° at 8° C/min, followed by an indefinite hold at 280° C. Two of the samples showed no detectable compounds. Other two produced very complex chromatograms.

It was deduced that the compounds observed in these samples resulted from the carrier oil associated with various herbicides.

Identification of individual species was made based on molecular weight and isotope distribution. Since some of the compounds of interest in the study contained chlorine, high confidence can be placed in their identifications. A sample collected in a previously identified area of herbicide contamination was used to develop a reference spectrum. This spectrum was used to define possible herbicide contamination. In order to provide another means for the identification of individual species, desorption GC/MS analysis is conducted.

Flux Mapping

The process of mapping the fluxes of compounds at the various sample locations is totally computerized. The sites on the map were digitized as X-Y coordinates after which various flux data for given compounds are plotted at these respective locations. The data was then contoured or highlighted. A typical contaminant flux map is shown in Figure 4.

A total flux map was prepared to show the sum of all contributing fluxes.

The flux value in the highly contaminated area was in the million ion count region. As previously mentioned, the ion counts represent relative fluxes and not an absolute value. Most of the other sample locations, with the exception of the samples located on the extreme south and north sides of the survey, had flux levels less than 500,000. This map gave an overall assessment of flux without species discrimination.

Compounds mapped separately included alkyl aromatic fluxes, to indicate the areas of herbicide carrier oil contamination; hydrocarbon fluxes, to assess the area for possible gasoline spills; and α-pinene flux, a compound resulting from vegetation, trees and brush. In this case, the use of a non-discriminating detector could have potentially lead to anomalies which were only contaminated by natural emission.

Other Compounds

In addition to the compounds mapped, trichloroethane, trichlorethylene, creosote, trithion, 2,4-D, DDD and chloroform were also considered as potential contaminants at the site. None of these compounds was detected at any of the sampling sites. The trithion, 2,4-D and DDD were probably at low enough levels in the contaminated area that they were masked by the carrier oils.

Conclusions

The data generated from the soil contamination investigation program support the following conclusions:

1. The presence of herbicide carrier oils, tetrachloroethylene, α-pinene and hydrocarbons were detected on the site.

2. The major area of herbicide contamination based on the presence of the carrier oils was defined. The area does no affect a large area within the survey.

3. The survey allowed the Consultant to define the extent of clean-up needed, the recommended cleanup method, the additional data requirements and the safety precautions during cleanup.

4. The Petrex static collection system can collect contaminant objects of this study and when analyzed by mass spectrometry indicate the presence of potential contaminants.

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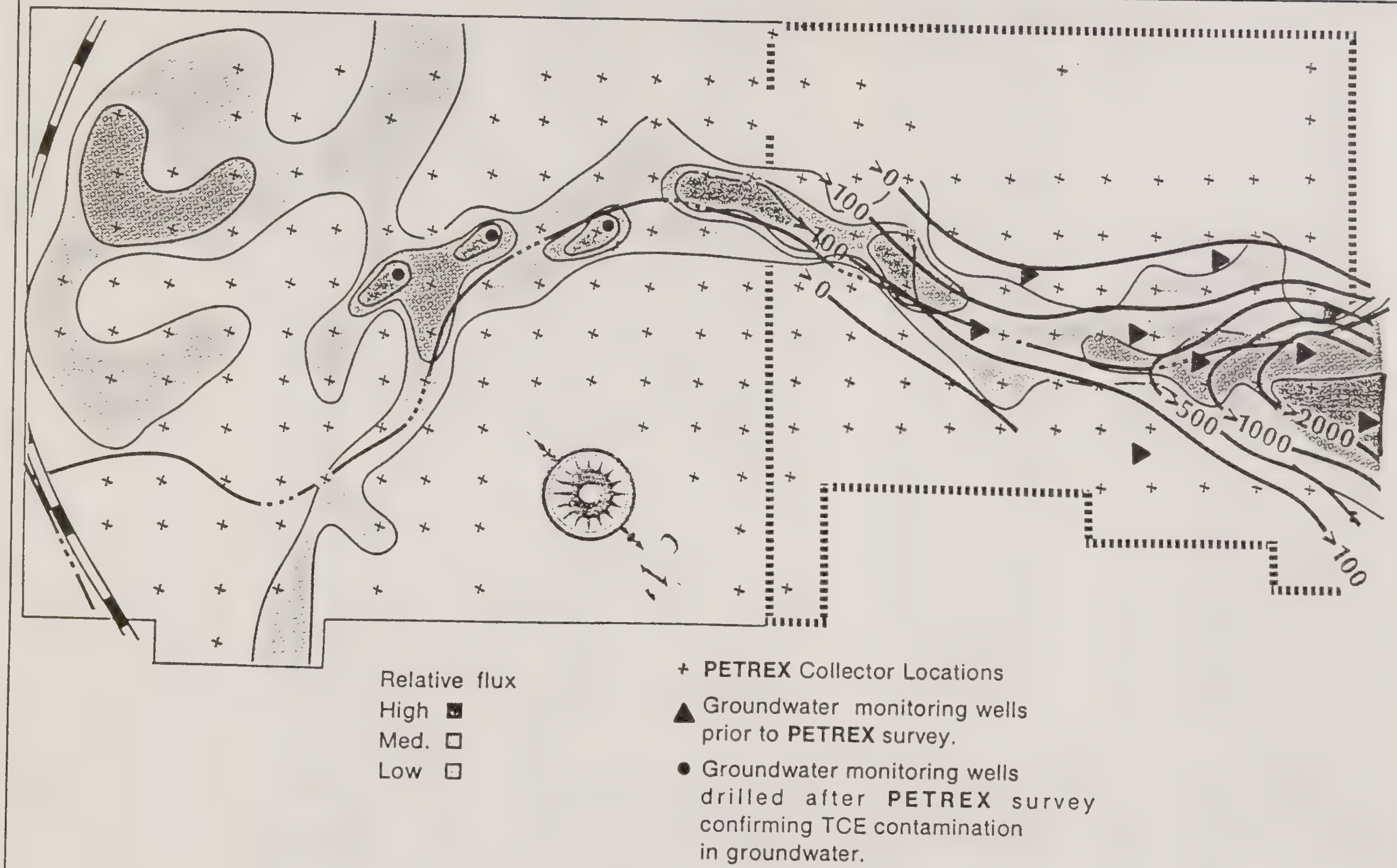

FIGURE 4: Relative Contaminant Flux In Soil

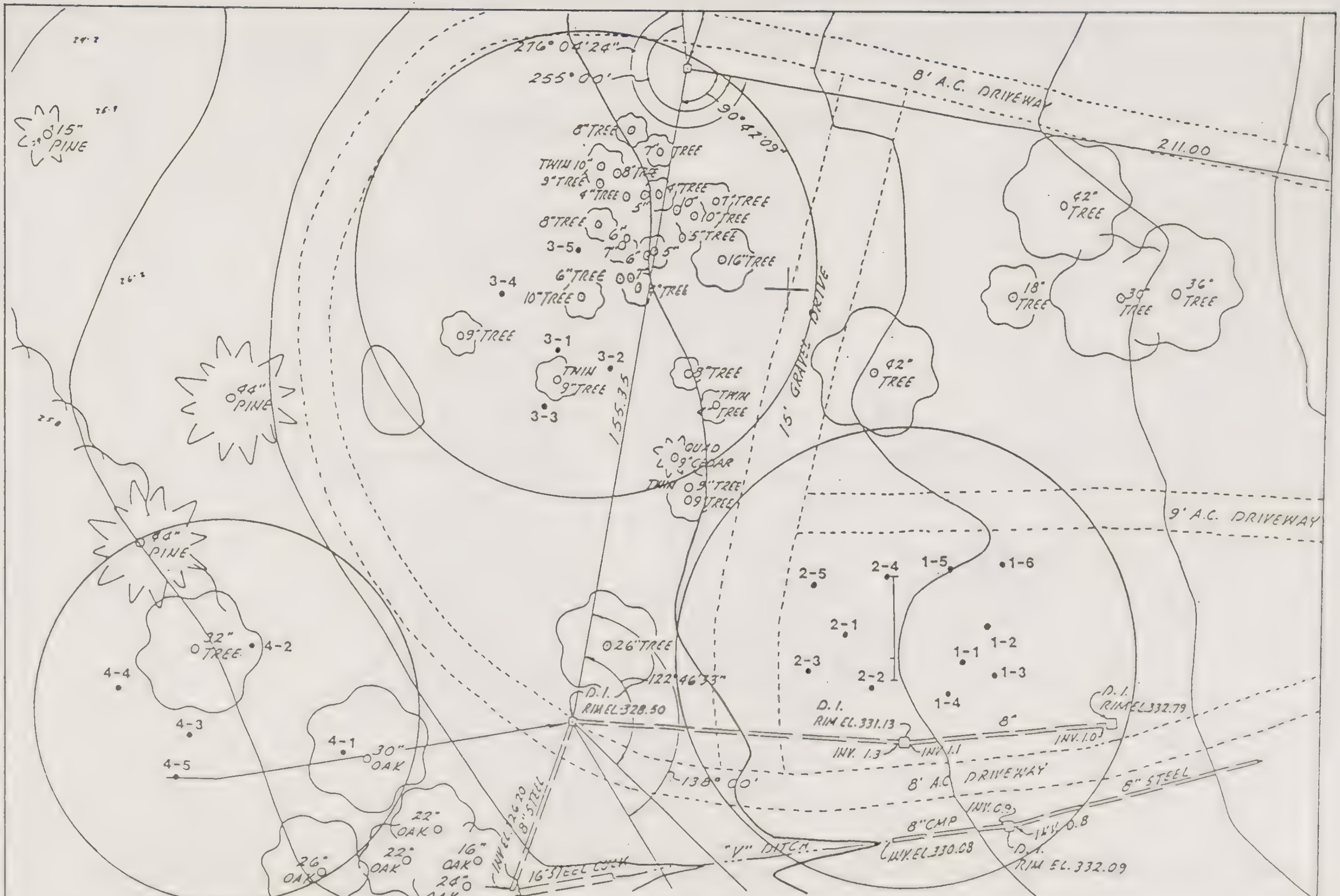

FIGURE 3: Sample Location Layout

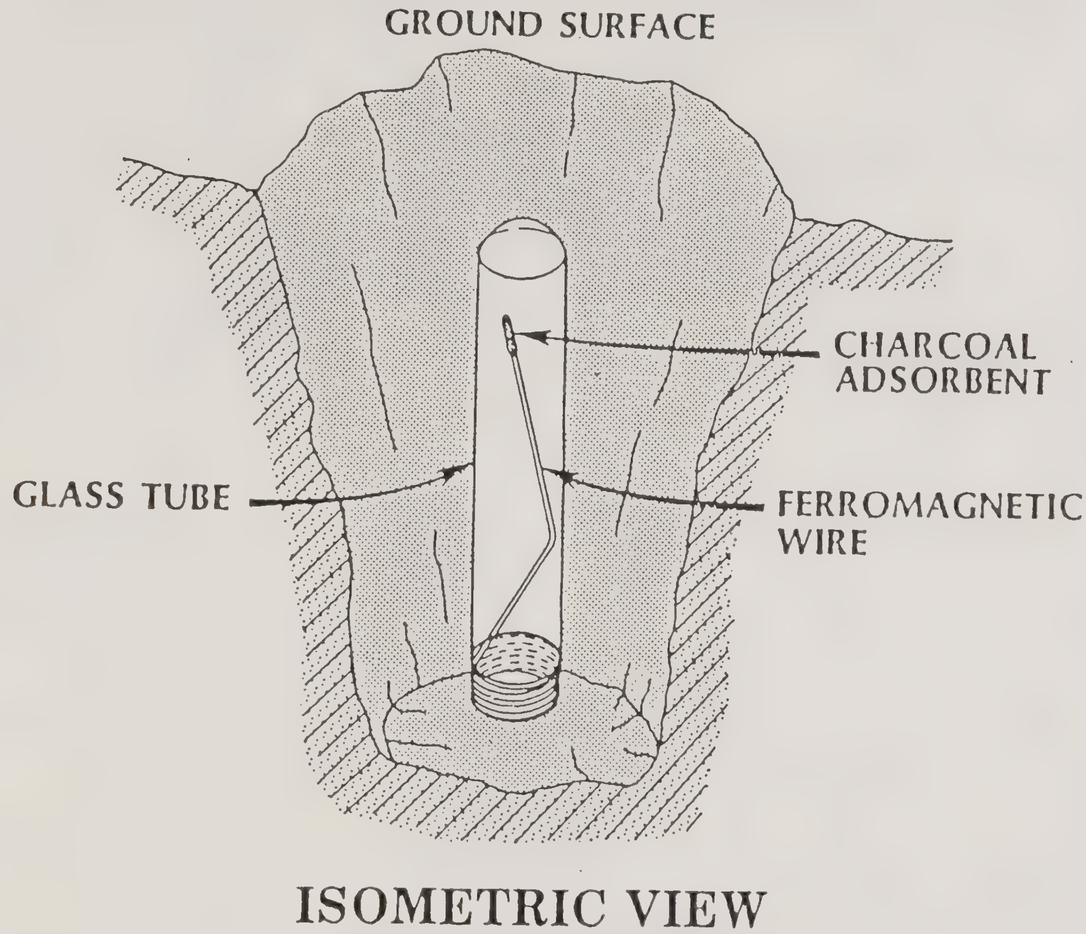

FIGURE 1: Schematic Diagram of Static Collector Used For Trapping Volatile Organic Compounds

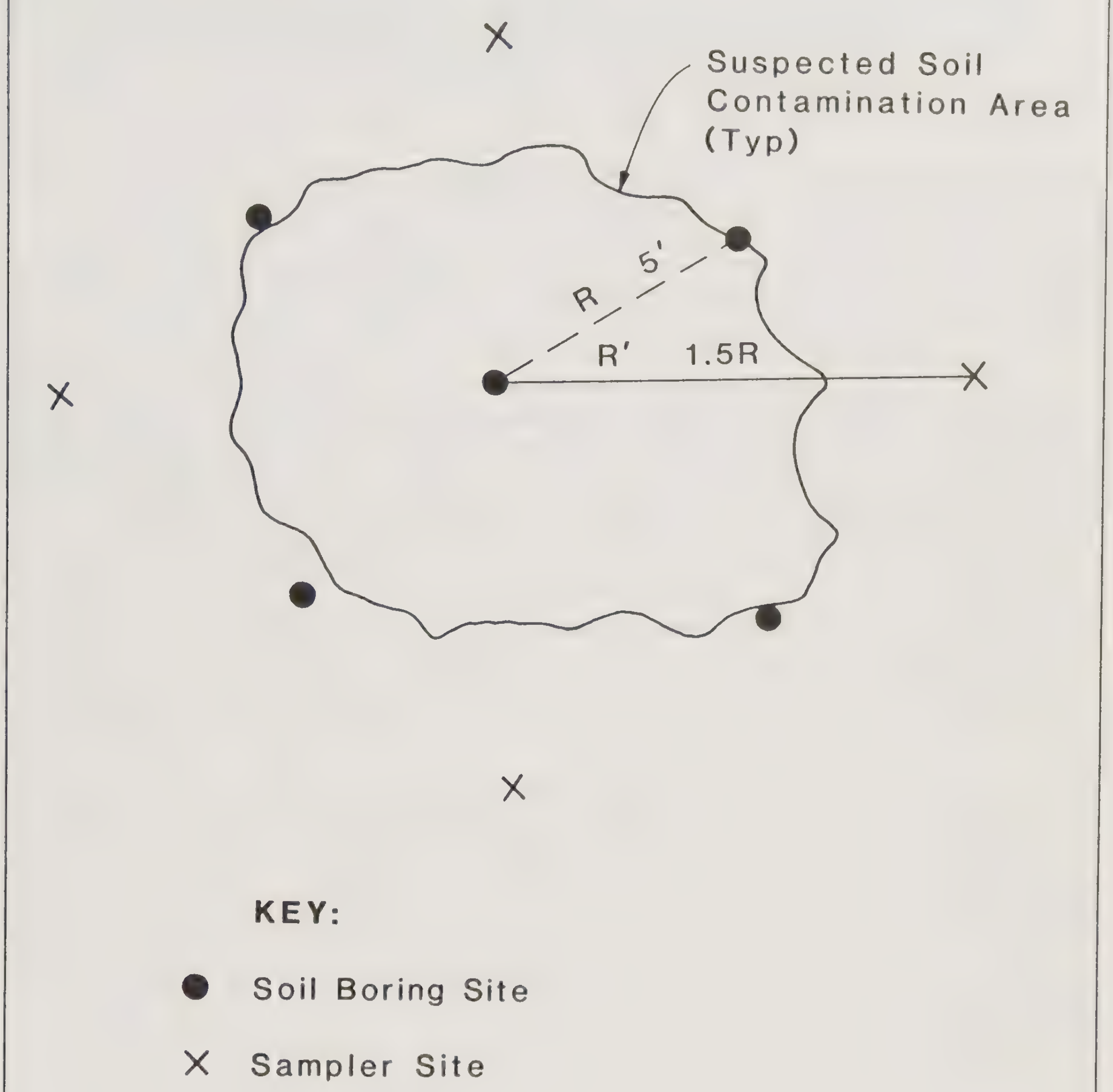

FIGURE 2: Typical Sample Location Procedure

Abstract

WASTE CLASSIFICATION AND CLEANUP LEVEL DETERMINATION

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Current California regulations do not specify in detail how wastes are to be classified and how cleanup levels for contaminated sites are to be determined such that all beneficial uses of waters of the State are protected. Staff of the Central Valley Regional Water Quality Control Board is currently developing guidance which aims to fill this regulatory need.

Improper waste disposal practices and sites which have been contaminated with toxic substances pose significant threats to the quality of California's useable ground and surface water resources. The classification of wastes and the establishment of cleanup levels for contaminated sites are performed by two separate State agencies with separate regulatory authority. The Department of Health Services classifies wastes as 'restricted hazardous' or 'hazardous' and sets cleanup criteria based on a direct threat of these wastes or soils to public health. The State Water Resources Control Board, together with the nine Regional Water Quality Control Boards, classify wastes as 'designated', 'nonhazardous solid', or 'inert' and determines cleanup criteria based on the threat that these wastes or soils pose to the beneficial uses of waters of the State.

Regulations administered by these agencies clearly state, using detailed criteria, how wastes are to be classified, with the exception of the 'designated waste' category. The lower boundary of this category is described only as the limit above which a waste could significantly impair water quality. Staff of the Central Valley Regional Water Quality Control Board is currently developing the Designated Level methodology which aims at more clearly defining this boundary. The boundary is defined in the methodology by the establishment of Designated Levels for specific constituents of a waste. Designated Levels are calculated by first establishing 'water quality goals', which are based on background water concentrations or accepted criteria and standards, and then applying factors to account for environmental attenuation and bioavailability. The result is a set of Soluble and Total Designated Levels which are applicable to a particular waste and disposal site, and which, if not exceeded, should protect the beneficial uses of waters of the State. Wastes having constituent concentrations in excess of these Designated Levels are classified as 'designated wates' and directed to waste management units which isolate these wastes from the environment.

It can be shown that the threat posed to water quality by contaminated soils is closely related to that posed by wastes in an unlined landfill, surface impoundment, or waste pile. As such, cleanup levels can be calculated, which will protect the quality of nearby ground and surface waters, in the same manner as Designated Levels are determined. As always, the background concentrations of contaminants must be factored into the cleanup level setting process.

When combined with the waste classification and cleanup level setting systems used by the Department of Health Services, the Designated Level methodology can provide a complementary package that should ensure the protection of both the public health and the quality of useable waters of California.

EXECUTIVE SUMMARY

The classification of wastes and the establishment of cleanup levels for sites which have been contaminated with toxic chemicals in California are performed by two separate State agencies with separate regulatory authority. The Department of Health Services classifies wastes as 'restricted hazardous' or 'hazardous' and sets cleanup criteria based on a direct threat of these wastes or soils to public health. The State Water Resources Control Board, together with the nine Regional Water Quality Control Boards, classify wastes as 'designated', 'nonhazardous solid', or 'inert' and determines cleanup criteria based on the threat that these wastes and soils pose to the beneficial uses of waters of the State.

Regulations administered by these agencies clearly state, using detailed criteria, how wastes are to be classified, with the exception of the 'designated waste' category. The lower boundary of this category is described only as the limit above which a waste could significantly impair water quality. This boundary can more clearly be defined by the establishment of Designated Levels for specific constituents of a waste. Designated Levels are calculated by first establishing water quality goals, which are based on background water concentrations or accepted criteria and standards, and then applying factors to account for environmental attenuation and bioavailability. The result is a set of Soluble and Total Designated Levels which are applicable to a particular waste and disposal site, and which, if not exceeded, should protect the beneficial uses of waters of the State. Wastes having constituent concentrations in excess of these Designated Levels are classified as 'designated wastes' and directed to waste management units which isolate these wastes from the environment.

It can be easily shown that the threat posed to water quality by contaminated soils is closely related to that posed by wastes in an unlined landfill, surface impoundments, or waste pile. As such, cleanup levels can be calculated, which will protect the quality of nearby ground and surface waters, in the same manner as Designated Levels are determined. As always, the background concentrations of contaminants must be factored into the cleanup level setting process.

When combined with the waste classification and cleanup level setting systems used by DHS, the Designated Level methodology can provide a complimentary package that should ensure the protection of both the public health and the quality of useable waters of California.

THE RELATIONSHIP BETWEEN SITE CLEANUP LEVELS, ENVIRONMENTAL FATE, AND EXPOSURE CRITERIA USING THE DOHS DECISION TREE

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INTRODUCTION

The mitigation of uncontrolled hazardous waste sites is one of the major challenges of this decade. Issues to be resolved as part of the site remediation process include assessment of the need for cleanup, establishment of site mitigation objectives, adequacy of site data, and appraisal of the existing and potential risks to public health and the environment.

The California Site Mitigation Decision Tree Process was developed by the California Department of Health Services, Toxic Substances Control Division, to provide a consistent, comprehensive, and systematic approach to site assessment, risk appraisal, and selection of remedial action strategy, based on sound scientific judgment and protection of public health and the environment. In recognition of the diversity and the complexity of hazardous waste sites, the Decision Tree Process emphasizes a series of decision-making steps, rather than a fixed approach, for each phase of the site mitigation process.

OVERVIEW OF THE DECISION TREE PROCESS

The Decision Tree Process provides several unique approaches to site mitigation and addressing the question of "How clean is clean?". The concept of an Applied Action Level (AAL) has been developed to define exposure criteria which are applicable statewide and are specific to a medium of exposure-- water, air, soil, or biota --and a biologic receptor--humans or a particular aquatic or terrestrial species.

The central feature of the Decision Tree approach is the development of site mitigation objectives based upon existing or potential exposure of a biological receptor to toxic chemicals. Environmental fate components of the Decision Tree are used to define the migration of toxic chemicals between environmental media, to evaluate off-site concentrations in a particular medium when on-site

concentrations are known, and to evaluate the relationship between known concentrations in contaminated media, such as soil, and potential concentrations in groundwater or air. Since concentrations to which receptors may be exposed are likely to differ from the on-site concentration in the contaminated medium, the site mitigation criteria is generally not equivalent to the AAL.

The selection of the preferred remedial action strategy is ultimately made by regional managers subsequent to consideration of nontechnical factors such as economics, land use, and public input as well as site mitigation objectives identified by means of the Decision Tree Process. The Decision Tree approach emphasizes the broad range of available remedial action strategies by referring to "site mitigation objectives" rather than "cleanup levels".

The Decision Tree Process also clarifies the distinction between site mitigation objectives and waste classification criteria. Waste classification criteria are intended to address the hazards associated with the various phases of waste management including disposal in a municipal waste landfill and do not adequately consider site-specific characteristics and their influence on attenuation factors between soil and groundwater.

COMPONENTS OF THE DECISION TREE PROCESS

The Decision Tree Process consists of five basic components: 1) Preliminary Site Appraisal; 2)Site Assessment; 3)Risk Appraisal; 4)Environmental Fate and Risk Determination; 5)Development of Site Mitigation Strategies and Selection of Remedial Action.

Preliminary Site Appraisal and Site Assessment

The Decision Tree provides specific guidance regarding preferred data-gathering techniques for the preliminary site appraisal and site assessment phases. The primary objectives of an adequate site assessment are identification of toxic chemicals present at the site, the spatial extent of existing contamination in the various environmental media (soil, water, air, and biota), and site-specific characteristics which influence the migration of contaminants. Examples of site features to be described in the site assessment include soil properties such as porosity and permeability, local geologic and hydrologic characteristics, direction of groundwater flow, and local meteorologic conditions. In addition, data should also be obtained from off-site areas in the vicinity of the site to define "regional background" levels of the chemical contaminants.

Environmental Fate

Environmental fate is an integral component of the Decision Tree process. The focus of the environmental fate component is to estimate the significance of and concentrations in exposure pathways for which no data exists using equiilibrium relationships between soil, water, air, and biota, atmospheric emission rate estimates, and air dispersion equations. Site data are necessary to derive a meaningful understanding of the interrelationship between environmental media. The use of site-specific data is essential to the Decision Tree approach.

Assessment of the migration between environmental media and between on-site and off-site concentrations is essential to the determination of exposure levels of the toxic contaminants to biologic receptors. The concentrations at the biologic receptor generally differ from, and are less than, those in the contaminated media on-site. The environmental fate component of the Decision Tree, together with the site assessment, provides the data necessary to evaluate the present or future concentration at the receptor.

Risk Appraisal and Risk Determination

The primary objectives of the risk appraisal and risk determination components are the assessment of whether existing or potential biologic receptors are currently or may in the future be at risk of adverse effect as a result of exposure to contaminants originating at the site.

The Applied Action Level (AAL) has been developed to define the statewide exposure criteria applicable to mitigation of uncontrolled hazardous waste sites.The AAL delineates a concentration in a particular medium which may pose a risk of an adverse effect to a specified biologic receptor. The AAL is derived from existing toxicologic and epidemiologic data and forms the scientific basis for selecting site mitigation objectives for compounds which are non-threshold agents (such as known and suspect carcinogens) as well as threshold agents.

To determine whether biologic receptors are at risk ,it is necessary to identify potential exposure pathways and whether concentrations at the receptors exceed AAL values. The pathways of concern are based upon chemical properties--such as mobility and volatility-- demographic patterns, and the use of resources such as groundwater and surface water.

The risk appraisal component takes into account exposures from multiple pathways and exposures to several compounds with the same toxicologic effect and mechanism of action.

Development of Site Mitigation Strategies and Selection of Remedial Action

The last component of the Decision Tree process has been derived principally from the U.S. E.P.A. process of selecting remedial alternatives for federal Superfund sites.

The selection of the preferred remedial action alternative is based upon site mitigation objectives derived by the Decision Tree process and in consideration of nontechnical concerns such as public input and economic considerations.

Site mitigation objectives are based on protection of existing and potential biological receptors from exposures exceeding AAL levels. In most cases, however, the site mitigation objective, or "cleanup level", for soil would not be expected to be the same as AAL values, which have been developed for air or water. Development of a site mitigation objective for soil would involve an identification of the potential exposure pathways and an understanding of the environmental fate to identify a soil concentration which would not result in an exceedance of the AAL value in an exposure pathway.

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PUBLIC/PRIVATE PARTNERSHIPS IN ELIMINATING BARRIERS TO PRODUCTIVE RE-USE OF CONTAMINATED SITES

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INTRODUCTION

There has been an increasing interest in the redevelopment of sites currently or formerly occupied by industrial or commercial uses, for such new uses as office buildings, retail and housing. Many large scale industrial facilities including, for example steel plants and refineries, have become outmoded due to economic changes. In addition, in many areas there are large tracts of land originally used for transportation activities, including rail yards, that are no longer needed for those purposes.

At many of these sites, materials which we now know to be hazardous when released into the environment were handled or generated. Because of the lack of concern about the hazardous properties of these substances, and the lack of effective regulatory controls over their handling or disposal, many of these materials were either intentionally disposed or inadvertently released at these sites. This has resulted in the contamination of buildings, soil, and in some cases ground water. At thousands of sites, underground tanks may have leaked chemicals into the soil. In some cases, otherwise vacant sites may have been used for illicit "midnight dumping".

The existence of a contamination threat may not be obvious. The contamination may be found beneath existing structures, or may result from a past activity which is unrelated to the present use. In many cases, the contamination will not be discovered until there is some interest in developing the site for a new purpose.

It is impossible to estimate reliably the number of contaminated sites which exist throughout the country. Based on various reports, EPA has assembled a list of 21,000 potentially dangerous sites under the Emergency and Remedial Response Information System. It is very probable that only a small percentage of the total contaminated sites have been identified. The General Accounting Office has predicted

that more than 378,000 sites eventually may require remedial action./1/

The issue of hazardous substance contamination is a relatively recent one. Attention so far has been directed primarily at waste disposal sites which threaten neighboring populations, especially by the migration of contaminants into groundwater. The focus of concern at these sites has been the elimination of threats to public health and the environment. There has been little consideration of how contaminated land can be recycled for more productive uses.

MAJOR PROBLEMS ENCOUNTERED IN DEVELOPMENT OF CONTAMINATED LAND

A person who intends to develop a project on a site which is to some degree contaminated with hazardous materials is confronted with at least four special problems. First, a substantial expense may be required to investigate the site and to carry out remedial action before the project can proceed. Second, it may be necessary to obtain some governmental review or approval for the remedial plan, or for the intended land use, because of the presence of contaminated material. Third, remedial action and/or governmental review may delay a project in many cases. Finally, the fact that a site is identified as contaminated may impact on the ability of the developer to market a project to potential purchasers or occupants. Two of these issues - cost and governmental review - will be discussed in more detail below.

While a developer wishing to purchase property can and should check the issues listed above before completing the transaction, a person who already owns a potentially contaminated site usually doesn't have the same options. If the land is endangering health and the environment, the owner may be ordered by local, state or federal agencies to clean it up. It may also be difficult, if not impossible, for the owner to dispose of contaminated property and the associated liability for clean up. Even if a sale is consummated, the seller may remain liable./2/ In some cases, despite the

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/1/ "A Problem that Cannot be Buried" Time, October 14, 1985, p. 76.

/2/ For example, the seller could be a "responsible party" under CERCLA for cost-recovery purposes under section (Footnote Continued)

difficulties in developing a contaminated site, an owner may proceed to minimize his liability or salvage what he can of his investment. In other cases, the owner may delay any cleanup liability by maintaining the site as is.

Costs of Dealing With Contamination

If contamination is suspected or identified at a site, a variety of expenses will be incurred before development can proceed. The nature of the contamination must be defined by sampling and analysis. A determination must be made as to whether remedial action is necessary, and if so, a remedial plan developed (and possibly, reviewed by a governmental agency.) Then, the remedial action (usually involving some combination of off-site disposal, on-site containment and/or on-site treatment) must be carried out. In addition to the costs of the remedial action *per se*, the developer will be required to pay for the services of a variety of professionals (soil engineers, toxicologists, economists and attorneys) to develop and obtain approval of the remedial action plan and to address any special problems raised in obtaining approval of the project. The costs will vary widely, but can be very significant - in some cases exceeding the market value of the site in an uncontaminated condition/3/.

For the majority of the contaminated sites, these remedial costs will be borne by the developer, and directly or indirectly by the previous owner of the property. Although the federal Superfund Program will be spending billions of dollars to address contaminated sites, those funds will be directed at a relatively limited number of the highest priority sites as designated on the National Priority List (NPL), or the other sites which present a more immediate threat and which can be mitigated (at least temporarily) at a relatively low cost. To date, EPA has evaluated approximately 10,000 sites to determine if they merit inclusion on the NPL; only 850 sites have been determined sufficiently serious, according to the EPA Hazard

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(Footnote Continued)
107. In addition, the seller may be liable to the purchaser if he fails to disclose or misrepresents the existence and nature of the contamination.

/3/ For example, in 1980 developers purchased a site in San Francisco for about $1 million in order to develop a residential project, apparently with little or no awareness of the nature of the contamination. Over $1.5 million was spent on the cleanup before the project could proceed.

Ranking System to be included on the proposed or final NPL./4/ California, and some other states, also have significant programs for cleanup of hazardous sites. Again, these programs will focus on the highest priority sites. For most contaminated sites, there may never be governmental funds available for remedial action, and it may be years before these programs address even all the high priority sites./5/

Of course, even if a site is not on the NPL or state priority list, federal, state and local governments have authority to compel a property owner (and other legally responsible parties) to take remedial actions. In theory, many sites might be cleaned up and made available for purchase and development. However, federal, and probably most state, enforcement resources will be for the foreseeable future, directed primarily at the sites listed on the NPL and state priority lists. Even when enforcement resources are available, remedial action will depend on the existence of some legally responsible party with the financial resources to pay for the cleanup. And even when there is such a party, there may be years of legal battle before the cleanup actually occurs.

Finally, even if there is a government funded cleanup, or a responsible party cleanup induced by legal action, the remedial action may not be adequate to allow development of the land. The Superfund standard for a cleanup is the most cost-effective action that adequately protects health and the environment. If the contamination can be safely contained, this standard would not require it to be completely removed or eliminated; additional expenses could be required to allow the productive use of the property.

/4/ Environment Reporter, Bureau of National Affairs, (September 20, 1985, p. 902)

/5/ The nature of the hazard ranking formula used by EPA in identifying sites for the NPL may reduce the possibility that many of the urban sites with high development potential will be given a high enough score to warrant inclusion. The formula is weighted to favor selection of those sites which pose an actual or potential threat to groundwater; where groundwater in the vicinity of the site is not used (as is true in many urban areas) the score is significantly reduced. Sites posing only "direct contact" threats from potential human exposure to contaminated soil may receive a relatively low score.

Governmental Review and/or Approval

There are several situations in which a person seeking to develop contaminated or potentially contaminated property may need special approval by some level of government. First, statutes and regulations may require approval before development can proceed. Second, a person may seek review because of the risk that some agency may eventually focus on the contamination at the site, and the desire to avoid delay or project changes that may result. Third, even where the developer is satisfied, based on the advice of specialists he has hired, that there is no problem or that the remedial action is adequate, the developer may seek governmental review to satisfy lenders, potential customers, and the general public that a project is safe. Finally, in some cases governmental approval of the remedial plan may enhance one's ability to recover costs from other responsible parties. The remainder of this section will identify several requirements/mechanisms for governmental review, and some of the problems and opportunities they present.

Federal Government - Unless the site in question is on the NPL, or is subject to closure requirements under RCRA, there is no requirement to seek federal approval for remedial action, although the owner may be required to notify the government if contamination is found. While owners of contaminated sites may in many cases wish to obtain federal approval of remedial actions for contaminated properties, there is no formal mechanism for obtaining such approvals. Federal resources are stretched very thin in addressing designated NPL sites, and it will generally be difficult or impossible to obtain federal review for other sites./6/

California - California has enacted several laws which may in some circumstances require state review before a person can proceed to develop or undertake remedial action for contaminated or potentially contaminated properties. Even when review is not required by state law, these provisions provide mechanisms for obtaining state review of the need for and terms of remedial actions.

Under a provision of Health and Safety Code (Division 20, Chapter 6.5 Article 11), if a person intends to construct building for certain uses (including residential) and

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/6/ "Participation of Potentially Responsible Parties in Development of Remedial Investigations and Feasibility Studies Under CERCLA", EPA Memorandum, March 20, 1984 at page 6. Review may not be available even for all NPL sites.

knows or has cause to believe that a "significant disposal of hazardous waste" has occurred on or within 2,000 feet of the site, he must apply to the Department of Health Services (DOHS) for a determination of whether the land should be designated a "hazardous waste property" or a "border zone property". Neither the law nor regulations provide a clear definition of what constitutes a "significant" disposal of hazardous waste.

DOHS can determine that there is no currently known hazard at the site or initiate the process of designating the land, "hazardous waste" or "border zone" property. The statute does not state how long DOHS has to complete its review. Once DOHS initiates the process of designating the affected land, a hearing must generally be held within 30 to 90 days. If DOHS determines that the land should be designated a "hazardous waste" or "border zone" property, it can act to severely restrict future uses of the site.

Experience under this provision is very limited. DOHS initially focused on sites already identified as contaminated with hazardous wastes, such as Superfund sites. To date, although some owners have voluntarily imposed deed restrictions, DOHS has not designated any site as through the hearing process. There is no regular flow of applications, and DOHS has made little effort to enforce the application requirement. The extent to which property is being developed in contravention to this requirement is unknown.

According to DOHS staff, at the present time a person could obtain a "no hazard" determination through this process in several months. Thus, at present, a person could satisfy the requirement and obtain a statement that no significant contamination exists, in a relatively expeditious manner. Increased state enforcement efforts, possibly combined with local pressure on developers to seek state review, could increase the volume of applications sharply, and slow down the process.

Another mechanism for obtaining review of a contamination problem is provided within the California Hazardous Substance Account Act (Health and Safety Code, Division 20, Chapter 6.8). Section 25356.1 of the H&SC provides that the DOHS, or Regional Water Quality Control Board ("Regional Board"), shall approve remedial action plans (RAP) for sites on the state priority list. In addition, section 25356.1(b) provides that a potentially responsible party <u>may</u> request DOHS or the Regional Board to approve a RAP for any other site if DOHS or the State Water Board determines that an action is required to respond to a release of a hazardous substance. The agencies must respond to a request to approve a RAP within 90 days of receipt.

Before adopting a final RAP, DOHS or the Regional Board must approve a draft RAP and circulate the draft for public comment for at least 30 days, and meet with concerned agencies, the potentially responsible parties, and the public.

In theory, this process should provide a relatively expeditious review, allowing the developer to proceed with the remedial action and construction of the project. In fact, the process may take more than the 90 days provided. First, the request for approval of a RAP may trigger requests for additional information from the developer. Second, once the necessary information is submitted to DOHS or the Regional Board, the agencies may lack the resources to complete the review within the 90 day period. Even if the process is working well now, the volume of requests may increase. The statute does not address what happens if the agency fails to respond within this 90 day period. Apparently, the remedy would be for the party to seek a writ in the Superior Court to compel the agency to complete its review.

The California Environmental Quality Act (CEQA) requires preparation of an EIR for all projects which a state or local agency carries out or approves which may have a significant impact on the environment (California Public Resources Code Section 21100, 21151). Development of a potentially contaminated site could result in an impact on the environment by allowing the release of contamination beyond the site, or bringing more people to the site to be exposed. Although the state CEQA Guidelines do not address the issue specifically, and there is no case law that I am aware of, it seems reasonable that in at least some cases presence of contamination would be a basis for requiring an EIR, and that contamination issues should be addressed when an EIR is prepared. The EIR process also provides a mechanism for addressing hazardous contamination issues. For example, the EIR for the San Francisco housing site mentioned above (note 3) outlined steps to be taken to mitigate hazardous contamination, and the city Planning Commission incorporated these as conditions to its authorization of that project (Resolution 9037, July 9, 1981).

<u>Local Agencies</u> - In general, local governments have not adopted any specific requirements addressing the development of potentially contaminated properties. However, the San Francisco Board of Supervisors is considering an ordinance which would require a person seeking a building permit, for certain types of properties, to prepare a site history and perform a soil analysis. Based on the analysis, a determination would be made whether there was contamination which required remedial action before a building permit

could be issued. If remedial action was needed, the person seeking the permit would be required to either clean up the land so that the concentration of the materials fell below a quantitative standard, or seek approval of the RAP by a state or federal agency.

The current draft of the ordinance references the criteria for identification of hazardous wastes set forth in California Hazardous Waste Management Regulations, California Administrative Code Title 22, Division 4, Chapter 30, Article 11, to determine whether the site is "contaminated". It is questionable if these criteria (established for determining whether a material is a "hazardous waste") are appropriate to define what level of soil contamination requires remedial action. However, there are no generally recognized numerical criteria defining "how clean is clean" for contaminated soil. Therefore, because the City does not intend to assume the responsibility of determining "how clean is clean", the only alternative would be to require each person performing a soil analysis to request a state determination either that no remedial action was necessary at a site, or approval of each remedial action.

The effect of this proposed ordinance may be to add significant delay to the process of developing land which is actually or potentially contaminated. Developers/property owners would lose the option of undertaking development or remedial action without seeking government review. Furthermore, it would substantially increase the RAP review burden on state agencies, perhaps slowing the process substantially.

PROMOTING DEVELOPMENT OF CONTAMINATED PROPERTY

For some sites, the special problems that must be addressed in development of contaminated property will be overcome without any special effort by government. Also, there are likely to be some sites for which the problems will be so severe that no conceivable set of government and private actions will result in productive reuse of the land. What we are concerned about here are sites between these extremes - those which might be developed <u>if</u> state and local decision makers act to provide incentives or remove impediments to doing so.

<u>Mitigating the Impact of Cleanup Costs</u>

If the developer determines, prior to purchasing property, that the cost of development (including remedial action to address contamination) is likely to exceed his expected return, the project almost certainly will not

proceed. Whether the cost of cleanup will render a project uneconomical will depend on the magnitude relative to the size of the project, and the expected return. Remedial costs of a million dollars might be supportable by a large project, although they would rule out a smaller one.

The locality should consider ways to make development of the contaminated property more feasible financially. The following are examples of steps which a local government could consider.

First, it could increase the allowable intensity of use for the site. Land use controls may operate to limit the size of buildings on the site. If the developer is allowed to build a larger structure, the ability to absorb remedial costs would be enhanced. The land use controls may have been adopted to serve legitimate purposes, but flexibility may be warranted in order to promote the development of a contaminated site.

Second, it may be necessary to modify the intended use of the contaminated property. For several reasons development of contaminated land for housing may pose special difficulties. The financial return to the developer from housing may be less than could be expected if the land was developed for other uses. In some cases a higher degree of cleanup may be necessary where land is to be used for residential purposes. For example, the City of San Rafael sought the development of a mixed use project that included a residential component. The site was found to be severely contaminated. It was determined that the cost of a cleanup sufficient to allow residential use would be approximately $50 million (for a piece of property with a value of approximately $5 million). However, if the land were to be used for commercial purposes only, a much less expensive cleanup would be adequate. Also, people are especially sensitive about potential contamination of their homes. It may be difficult to market such property even after assurances from government officials about the adequacy of the clean up.

Third, localities may improve the economic equation for development of contaminated land by reducing or eliminating some of the fees which a developer would otherwise pay in connection with the development. Developers are often required to dedicate property to public uses, or pay other fees or exactions. For example, a person who develops an office project subject to San Francisco's new Downtown Plan must pay fees for transit improvement, child care, parks, housing mitigation, etc. These fees and other requirements are estimated to add approximately $14.00 per square foot to the cost of new office space. Waiver of some of these fees where substantial remedial actions are needed to address

contamination could make a project on contaminated land economically viable.

Ideally, when local governments make plans for sites whose history suggests the possibility of contamination, they should factor the contamination issue into their planning. By so doing, they increase the chance that the plans will provide appropriate uses for given properties, and that the planned intensity of development will be realistic.

The financial problems of developers of contaminated properties could also be mitigated by not requiring remedial actions more expensive than those truly necessary to provide adequate protection. Even when a remedial plan is approved by EPA or a state agency, local agencies or elected officials may question the adequacy of the plan, especially where it involves leaving some contaminated material on-site.

The questions of "how clean is clean" and whether different technologies provide an appropriate degree of safety are often controversial. While citizens and local officials, of course, should participate in the process of reviewing clean up decisions, and point out problems, excessive or unfounded criticism of these agencies is harmful. Even if a State-approved RAP survives a challenge, unwarranted and baseless criticisms can damage the marketability of a project.

Even when a developer concludes that a project which requires substantial remedial action is economically viable, it may be necessary to assure that changes in land use regulation after the clean-up commences do not undercut the project. California law provides for "development agreements" to freeze land use controls for particular sites (Government Code, Article 2.5, Chapter 2.4 of Division 1 of Title 7). Local governments should be willing to enter such agreements for projects on contaminated sites.

Streamlining Review Procedures

Where government review is necessary, efforts should be made to streamline the process. In addition, unnecessary review should be avoided.

First, it may be necessary to provide additional resources to the responsible agencies to allow them to respond in a timely manner. Providing speedy review of RAPs for development projects would be in the public interest because it would enable sponsors to provide new housing, office, and retail facilities more quickly and at a lesser

cost. In addition, faster approval of RAPs could speed control of contamination.

In this era of governmental financial constraint, a substantial expansion of public expenditures in this area may be difficult. If state review is necessary, it may be useful, in recognition of the substantial benefits to project sponsors of speedier response to remedial action plans, to consider a system in which persons seeking approval of remedial action plans in connection with development of land would be assessed a fee for review of RAPs.

EPA and state agencies also could aid the review process by developing numerical criteria defining "safe" levels of soil contamination, for particular factual situations. Such criteria would speed the process for determining either that no remedial action was required or what clean up level should be achieved. In addition, the development of "no action" levels for hazardous substances in common situations might in many cases obviate the need for detailed governmental review of the remedial plan. For example, if such criteria were available, they would reduce the extent to which developers subject to the proposed San Francisco ordinance were required to seek state review. Of course, such criteria by their nature would have to be "conservative", adequate to provide sufficient protection in all situations to which of that they apply. Developers would still have the opportunity to seek approval of RAPs which did not achieve the criteria, if they could demonstrate, based on the particular facts, that the alternative provided adequate protection.

<u>Government-Funded and Enforcement Cleanups</u>

Where remedial actions are funded by government, or result from enforcement actions, the actions may not provide for the most optimal land use, from a local point of view. Local agencies must participate in the remedial selection process. If the nature of the "cost-effective" action would interfere with long-term goals for the site or general area, localities must be prepared to offer alternatives which do not increase federal or state remedial costs.

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CONTAMINATED SITE RESTORATION BY RESOURCE ENHANCEMENT

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ABSTRACT

Each year enormous sums of money are spent to restore potentially valuable real estate from contaminated conditions. More often than not, the contaminated soil and water are treated and/or disposed of with no thought given to their potential economic value. If economic uses could be found for these treated media or for the site areas, the costs of hazardous waste remedial actions might be reduced dramatically. This concept is called "resource enhancement". The arguments for this concept are persuasive.

In the United States today, thousands of potentially responsible parties (PRPs) and regulatory agencies conduct remedial investigations/feasibility studies (RI/FSs) at tens of thousands of hazardous waste sites. PRPs and agencies expect to spend millions of dollars at each site to restore them to background, regulatory-mandated, or lower receptor-risk conditions. Many sites are located on otherwise prime property at valuable locations: in cities; adjacent to piers, rails, and roads; and at industrial parks with full utilities. Billions of cubic yards of soil will be excavated, and trillions of gallons of groundwater will be pumped. Contaminated soil and water will be treated to remove or stabilize corrosive, reactive, toxic, ignitable, or specifically listed hazardous materials. Most of this treated soil and water is scheduled for no economic or practical use.

Opportunities include: treated groundwater for higher use; treated soil for higher use; soil excavation for subsurface structures; and site modification for higher use. Direct use of contaminated soil and groundwater may be possible in some cases. Enhancement may offer a pathway to generate useful products, competitive advantage, and even profits. More important, the concept would appear to be

cost-effective, reduce PRP liability, provide positive community relations, conform to regulatory incentives, and decrease regulatory burden.

Resource enhancement is technically, environmentally, and economically viable in many cases; cultural, institutional, and public policy issues are currently constraints. Higher land and water uses are especially attractive, as they can offset cleanup costs.

INTRODUCTION

RCRA, CERCLA, and numerous state measures[1] set the U.S. regulatory environment for the management of hazardous wastes at both controlled and uncontrolled waste management sites. Consequently, potentially responsible parties (PRPs) and regulatory agencies are conducting remedial investigations/feasibility studies (RI/FSs) at tens of thousands of hazardous waste sites in the U.S. today. PRPs and agencies expect to spend up to tens of millions of dollars at many of these sites to restore them to background, regulatory-mandated, or lower receptor-risk conditions. Many sites are located on otherwise prime industrial property at valuable locations: in cities and at industrial parks; adjacent to piers, rails, and roads, with full utilities. Billions of cubic yards of soil will need to be excavated, and trillions of gallons of groundwater will need to be pumped; contaminated soil and water will need to be treated to remove or stabilize corrosive, reactive, toxic, ignitable, or specifically listed hazardous chemicals. In most cases, this treated soil and water are scheduled for no economic or practical use, although it could be suitable for many uses with little or no modification in treatment.

Contaminated site restoration by resource enhancement means taking a hazardous waste site, with its contaminated soil and water problems, and making the site, its soil and water, more valuable than it was prior to restoration. Resource enhancement could pay for part of a site's cleanup costs and could make the difference between "breaking even" and "making a profit". This paper examines the potential for resource enhancement at hazardous waste sites.

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1 The Resource Conservation and Recovery Act (RCRA) of 1976 (40 CFR Part 270), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, or "Superfund") of 1980 (40 CFR Part 300) as amended and reauthorized, and state initiatives such as Subchapter 15, Chapter 3, Title 23 of the California Administrative Code and Article 9.5, Section 25208, Chapter 6.5 of Division 20 of the California Health and Safety Code.

RESOURCE ENHANCEMENT OPPORTUNITIES

In its broadest meaning, resource enhancement could be considered at every hazardous waste site subject to the RI/FS process. Opportunities might include: treating groundwater for higher use, treating soil for higher use, using excavations to accommodate subsurface structures, and tailoring site modifications for higher use. Additionally, already contaminated soil and water might be used directly in some manufacturing processes with little or no treatment.

At the national level, the annual unrecovered costs of site investigations, remedial action planning, and cleanup are not regularly reported, but surely must amount to several tens of billions of dollars. Tens of thousands of sites are subject to study or cleanup activities at any one time, and of this number, several thousand involve substantial volumes of treated soil and groundwater that could be candidates for the resource enhancement concept. The cost of treating and disposing of soil and groundwater at a "typical" site (including serial investigations and inspections) is typically on the order of several million dollars. (An example of a typical site is a five-acre parcel with volatile organic compounds in the soil at concentrations of 300 to 3,000 ppm, and the same compounds in the water at concentrations of 20 to 300 ppm.) A conservative estimate of the annual cost of cleanup of "typical sites" (assuming 5,000 sites at five million dollars each and a three-year term) is about ten billion dollars.

At the level of the individual site, resource enhancement may benefit owners and operators in several ways. First and most readily apparent, the ability to recover cleanup costs represents immediate savings and may make the difference between economic viability and failure. Second, maintenance of the economic value of sites by pursuing site modifications/excavations or by avoiding business failure or recession, will minimize write-downs or write-off of the substantial infrastructural investments common at most modern industrial facilities. Third, well-planned management of an onsite waste problem (by coordination with long-term facilities planning) will yield higher future values for rent and sale of land and improvements. Lastly, some of the costs of cleanup, restoration, and resource recovery correspond to tax savings, and perceptive advance planning of resource enhancement activities has the promise to generate profits that are in effect tax sheltered.

Clearly, our state and national laws are intended to protect the environment and the health and safety of the people, and are not written to make it easy on the PRPs who must clean up the waste. Any logistic manipulation to use these existing laws and regulations to make a profit out of an obligation to clean up contamination is going to be awkward. The theme of most waste cleanup laws (and agencies who enforce them) is that those who are responsible must pay for their

mismanagement, but why dwell on the assignment of blame, to the exclusion of good new ideas? Resource enhancement makes sense. Resource enhancement ought to be encouraged by our laws and institutions because it preserves resources and adds economic value primarily at a fundamental (versus service) level, where added value accelerates rather than retards economic growth.

Even though the present institutional-regulatory environment does little to promote resource enhancement, there are a number of readily apparent opportunities to achieve direct savings or cost recovery. With the impulse of legislated incentives (in the form of regulatory relief and/or tax incentives) creative entrepreneurial spirit is certain to expand and diversify the activities that embrace the resource enhancement concept. Some creative ideas for resource enhancement prospects (all possible under current laws) follow.

Treated Groundwater for Higher Use

Many hazardous waste site cleanups include the treatment of large volumes of contaminated groundwater. Treated groundwater could be used for cooling water, landscape or irrigation supply, chemical source supply, drinking water(?), and recharge to control salt-water intrusion in coastal areas or land subsidence in areas of large groundwater withdrawals.

The expense of purifying contaminated groundwater is usually very high. Cost figures published in the Federal Register have been as high as $1.50 per thousand gallons for relatively simple cleanup problems. At most hazardous waste sites, the treated water is discharged with no further use intended. In some cases, it is discharged to a Publicly Owned Treatment Works which may then charge for additional treatment before ultimate discharge to a receiving body.

After spending large amounts of money for a treatment plant to purify the water, there may be a higher use for that water. Uses as process water or cooling water can be considered at an operating site. In some cases, groundwater is used for irrigation in the vicinity of a site. Treated water might be used directly for irrigation or it might be recharged to the ground in such a way as to control salt water instrusion or land subsidence. In these cases, the water users who were threatened by a contamination problem may be benefitted by the operation of the treatment plant.

In some cases, it may be possible to upgrade the treatment to safe drinking water standards and achieve the higher use for municipal supply. A few hazardous waste sites are doing just that.

Treated Soil for Higher Use

Many hazardous waste site cleanups include the treatment of large volumes of contaminated soil. Treated soil (gravel, sand, silt, clay)

could be used for landscape and structural fill, grade, cap, or aggregate base material used in engineering projects.

If contaminated soil can be treated at a hazardous waste site to render it nonhazardous, at a minimum, it may be possible to eliminate the need to haul it to a secure facility. Furthermore, it may be feasible to upgrade the treatment process so the treated soil can be put to a commercial use.

For example, a gravely soil contaminated with a PCB-laden oil could be cleaned sufficiently to leave it in place for perhaps $80 per cubic yard. For an additional $15 per cubic yard, it could be enhanced to allow its use as a road-building material. The treated soil might have a value of perhaps $30 per cubic yard as a road-building material. Thus, a part of the site cleanup cost can be recovered by use of a resource enhancement outlook.

Soil Excavation for Subsurface Structures

Many hazardous waste site cleanups include the excavation of large volumes of contaminated soil. Excavation sites could be constructed so that they form the foundation for subsurface structures, storage areas, sanitary landfills, or other structures.

At many hazardous waste sites subject to the RF/IS process, the landuse activities that produced the hazardous waste situation have ceased. New uses for the site will often entail new construction. With sufficient foresight and planning, it may be possible to take advantage of soil excavations in the new construction plans. This could reverse the situation seen at some sites where an excavation, backfill, grading, and surfacing program is followed by a new project with foundations or other structures placed in the same location.

This aspect of resource enhancement can be seen as closely related to the next section on site modification.

Site Modification for Higher Use

Many hazardous waste site cleanups include major site modifications for excavations and fill. Sites could be modified for higher use, such as recreational fish ponds or other areas, warehouses, storage facilities, parking lots, parks, sanitary landfills, and storage yards.

As suggested in the introduction, many hazardous waste sites identified in the U.S. are in locations that should have a high intrinsic value. A number of these are on or very near bays, rivers, lakes, or the ocean. Past practice was to use these waterways for transportation of raw materials and products. With the increased pressure of encroaching population growth and the changes in shipping practices, many of these sites are far more valuable now for other uses.

The downside to this situation is that site cleanups may have to be especially thorough to permit uses of high return; but if the return is high, an expensive cleanup program may be justified. The point is largely one of outlook or attitude. Rather than trying to spend the minimum amount necessary to get off a site and still seeing a bill in the ten million range, it may be possible for the PRPs to consider a new use for the site and at least a partial recovery of costs if not a profit.

Direct Use of Contaminated Soil and Water

Many hazardous waste site cleanups must deal with large volumes of contaminated soil and water. Contaminated soil and water may be used directly in some manufacturing processes which do not require high quality source material, in other words, with little or no treatment. Potential uses for soils include aggregate for ornamental concrete or roadbeds. Promising processes for water include base material for industrial bleach, soaps, paints, and solvents. Perhaps modest amounts of petroleum derivatives may be compatible with manufacturing certain grade chemicals and paints.

RESOURCE ENHANCEMENT ISSUES

Resource enhancement is an attitude or approach which may offer a pathway to generate useful products and profits, be cost-effective, reduce liability, provide positive community relations, conform to regulatory incentives, and decrease regulatory burden. The potential for resource enhancement at hazardous waste sites is especially meaningful where site location, soil excavation, aquifer restoration, and soil and water treatment are favorable. Resource enhancement is technically, environmentally, and economically viable; cultural, institutional, and public policy issues are currently constraints. The technical, environmental, and economic uncertainties of resource enhancement are relatively easily resolvable, but require detailed analyses; the cultural uncertainties of enhancement may be more difficult to resolve. The costs of land and water uses make resource enhancement especially attractive, as they can offset cleanup costs.

Higher landuse is an important potential goal at many sites. This is because past practices frequently included contamination of land near water bodies of all types. Chemical plants, gas plants, and oil and chemical handling facilities were often located near rivers, bays, lakes, and the ocean. With higher population densities and new attitudes on landuse and transportation policies, many of these sites are potentially prime real estate. If an eyesore and public health nuisance can be converted to a public asset, the entire project can potentially be turned around economically as well.

A major concern in making resource enhancement possible will always be the assurance that the conversion is genuine. Without a credible

clean bill of health, the resource enhancement concept will fail. The conclusion is that resource enhancement will require three things that are often in short supply at a hazardous waste site: cooperation, trust, and planning.

A number of potentially constraining cultural issues are identified: insurance, liability, regulatory and legislative requirements, institutional limits, and public education. Who would be responsible if, in the long term, health problems arise and are attributable to a resource enhancement project? What insurance and liability issues must be solved? Would regulations and legislation on water quality standards permit such projects? Would the public - water consumers, irrigators, industrial and commercial interests, etc. - accept these projects? What institutional and public education policies need to be implemented to encourage successful projects? What public policies are needed to support the private sector to make such projects work? These issues will require careful analysis.

Viewed simply, contaminated site restoration by resource enhancement means taking a hazardous waste site, with its contaminated soil and water problems, and making the site, its soil and water, more valuable than it was prior to restoration. The concept appears viable for selective hazardous waste sites.

ACKNOWLEDGMENTS

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CLEANUP OF CENTURY-OLD WASTES AT AN URBAN CONSTRUCTION SITE

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INTRODUCTION

In October 1984, site preparation began for construction of a 23-story office building in downtown San Francisco. A dewatering system was installed prior to excavating for the building basement. When dewatering commenced in early February 1985, an oily material with a strong creosote-like odor appeared in the dewatering wells. Subsequent investigation revealed the presence of a 5-foot-thick layer of coal tar waste throughout the site, the top of which was approximately 10 feet below ground surface. Although the origin of the material was unknown at the time of discovery, the source was later determined to be an illuminating gas plant which had disposed of coal tar waste during the 1850s.

Removal of the entire waste deposit within the site was required during the foundation excavation process. Changes in construction activities were required in order to integrate the waste removal into the highrise construction process. This paper describes how the waste removal was safely accomplished within the confines of a highly congested urban construction site.

HISTORY OF THE WASTE DEPOSIT

The coal tar waste deposit at the site originated at the time of development of the San Francisco waterfront and resulted from an industrial process that predates the invention of the electric light.

Prior to the invention of the incandescent lightbulb, gas light was the most efficient form of illumination. Illuminating gas produced by the destructive distillation of coal was first used to light a home in 1792, and in 1812 the first manufactured gas plant was opened by the London and Westminster Chartered Gas, Light and Coke Company. The first American gas plant soon followed in Baltimore in 1816 (4). By 1920 there were 1114 gas plants operating in the United States, many of which utilized oil rather than coal (3). By that time the major use for manufactured gas had shifted from illumination to heating. During the 1950s, these plants were almost completely phased out

because they could not compete with less expensive natural gas (2).

Early plants produced gas by heating bituminous coal in cast-iron retorts. The gas, liquid coal tars, and ammoniac liquor were drawn off through a hydraulic main, leaving coke behind (1a). Because of their limited operating temperatures, iron retorts produced relatively low volumes of gas and a chemically rich coal tar mixture (1). Although higher temperature clay retorts capable of extracting larger volumes of gas were introduced in England in 1844, decades passed before they displaced iron retorts in America (1). The coal tars produced by early plants were usually disposed of at or near the plant sites as a matter of convenience. Although some limited early use was made of the tars as they came from the retorts, tar distillation was not established as a separate industry until the 1880s (3).

The first producer of illuminating gas in San Francisco was the San Francisco Gas Company, which was incorporated on August 31, 1852 (5). Between 1852 and 1854, a gas plant was built next to the San Francisco waterfront which ultimately occupied the area bounded by First, Natoma, Howard, and Fremont streets. City streets were first lit with gas on February 14, 1854 (6). As can be seen from Figure 1, the eastern end of the present South-of-Market area, including the project site, was known as Yerba Buena Cove during that period. The cove was shallow inshore, with broad mud flats along its northern rim and a sandy shoreline to the south (9).

In the early days of the plant's operation, waste coal tar was pumped through a 6-inch pipeline directly into Yerba Buena Cove at a point one block east of Howard and Beale streets (10,11). The accumulated waste soon formed a tarry surface visible at low tide, causing the area to become known as the Tar Flat (12).

Although the cove once supported a cockle and clam fishery, this was soon destroyed by the gas plant effluent. According to a nostalgia columnist in the early 1900s, "the cockles perished miserably and absolutely--helpless victims of the ocean immolated on the alter of light" (11).

In 1847, seven years before the opening of the San Francisco Gas Company plant, the tidelands of Yerba Buena Cove were subdivided into beach and water lots and sold at auction, including the project site (8). In order to reclaim these lots, an ambitious landfilling program was initiated which ultimately resulted in the complete filling of Yerba Buena Cove and the creation of the eastern San Francisco shoreline as it exists today. The sequence of filling is shown in Figure 1.

Coast survey maps show that the site was completely submerged in 1853. In 1857, it was an oval-shaped tidepool partially bounded by landfill and a Beale Street pier. By 1869, the cove area was completely filled (13). The waste deposit at the Tar Flat was buried

with the filling of the shallow water at the foot of Howard Street (10). It would not be recognized again for more than 100 years.

SITE CONDITIONS

The site is located several blocks from the San Francisco financial district and the San Francisco-Oakland Bay Bridge. It is square-shaped, 135 feet on a side. The remainder of the block is occupied by an L-shaped 9-story office building.

Subsurface soil conditions observed at the time of the foundation excavation are shown on Figure 2. The upper soil layer consisted of brown sandy fill from ground surface to a depth of approximately 15 feet, with tarry waste material occurring throughout the site in a layer between 10 and 15 feet below ground surface. Directly below the waste layer is the "new bay mud," the gray sandy silts which were the surface soils of Yerba Buena Cove in the 1850s. Below the new bay mud is a green silty sand.

Ground water was encountered in the fill approximately 10 feet below ground surface. The new bay mud, with a permeability of 4.5×10^{-5} cm/sec, appeared to act as a leaky aquitard, limiting the movement of ground water between the upper fill and the green silty sand.

The tarry waste layer contained a mixture of volatile organic hydrocarbons, polynuclear aromatic hydrocarbons (PNAs), and phenols. Principal constituents are shown in Table 1. Because this material is classified as a hazardous waste under California law, disposal at a permitted hazardous waste disposal facility was required.

The upper portion of the new bay mud layer contained many of the constituents found in the waste, but at much lower concentrations, as shown in Table 1. No contaminants were found in the lower green silty sand.

Because the new bay mud contained hazardous constituents in low concentrations, a petition for classification as a nonhazardous waste was submitted to the California Department of Health Services, Toxic Substances Control Division. Using the methodology described in Section 66696 of the California Administrative Code, an LD_{50} value of 14,606 mg/kg was calculated for the new bay mud. This material was shown to be less toxic than the 5000 mg/kg level which characterizes a hazardous waste, and the new bay mud was therefore designated nonhazardous. This designation allowed the new bay mud underlying the waste deposit to be disposed of at a sanitary landfill.

Ground water sampled from the upper fill layer also contained volatile organics, PNAs, and phenols, as shown in Table 2. The relative percentage of phenols was higher in ground-water samples, as would be expected from the greater water solubility of phenols. Ground water

Table 1. Typical Chemical Composition of Waste and Underlying New Bay Mud

Constituent	Concentration in Waste (ppm)	Concentrations in New Bay Mud (ppm)
Benzene	100	2.7
Ethyl benzene	160	9.2
Toluene	710	1.3
Methylthiophene	20	ND
Xylene isomers	1600	34
Tetrahydrofuran	120	ND
Acenaphthene	100	9
Acenaphthylene	650	39
Anthracene	450	28
Benzo(a)anthracene	400	17
Benzo(a)pyrene	10	ND
Benzo(b)fluoranthene	10	ND
Fluorene	550	46
Fluoranthene	450	17
Naphthalene	2300	70
Phenanthrene	1300	ND
Pyrene	550	51
Dimethyl naphthalene isomers	200	30
Methyl indene isomers	200	ND
Methyl naphthalene	2000	90
Methyl phenanthrene isomers	300	ND
Indene	500	ND
Phenols	400	43

from the lower green sand layer was found to contain 60 ppb phenols during an initial sampling; however, no priority pollutants were detected during a subsequent sampling after dewatering began.

DEWATERING

Because the foundation excavation was to extend at least 10 feet below the water table, dewatering was required before and during excavation. It was planned that the dewatering system would remove water from the fill layer prior to excavation, prevent inflow of water during excavation, and reduce hydrostatic pressure on the new bay mud layer to prevent bottom heave in the excavation.

The original dewatering system, designed and installed before the discovery of the waste, consisted of 24 sand drains connecting the upper fill and lower green silty sand, and eight pumping wells screened in the lower sand, with annular spaces sand-packed from the bottom of the hole to the ground surface. This system created a direct hydraulic connection between the waste layer and the uncontaminated lower green

Table 2. Chemical Composition of Ground Water in Upper Fill Layer

Constituent	Concentration (ppb)
Ethylbenzene	356
Toluene	500
1,5-hexadiyne	2930
2,5-dimethylthiophene	226
Trimethyl benzenes	2140
Xylenes	1085 (1)
2-methylthiophene	530
Benzofuran	3100
Naphthalene	790
Acenaphthylene	520
Phenanthrene	268
2-methylphenol	5560
2-methylnaphthalene	630
Benzofuran	2780
IH-indene	4770
3-methylphenol	7567
2,3-dimethylphenol	4921
Xylenes	4300 (2)
2,6-dimethylphenol	7885

(1) Identified in analysis of purgeable fraction.
(2) Tentatively identified in extractable fraction.

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silty sand, which was clearly illustrated by the appearance of tar in the wells when the system was first activated. Following discovery of the contaminated layer, it became apparent that the upper fill and lower sand layers would have to be re-isolated and dewatered separately to prevent the spread of contamination during construction. The dewatering system also took on added importance because of the need to remove free liquids from the waste prior to disposal at a hazardous waste disposal facility.

Re-isolation of the upper fill and lower sand was accomplished by pressure grouting the sand drains and wells with a sodium silicate grout mixture where they penetrated the new bay mud layer. Sand drains were grouted to complete closure. Wells were grouted only in the annular space to allow them to be used for selectively dewatering the lower sand layer.

A separate vacuum dewatering system was installed in the upper fill, consisting of 2-inch-diameter wells spaced 8 feet apart along the site perimeter, with additional wells inside the area to be excavated. The wells penetrated the upper few feet of the new bay mud

and were connected through a series of manifolds to a single vacuum pump. Dewatering wells are shown on Figure 2.

Prior to dewatering, ground water from the upper fill was tested for amenability to activated carbon treatment, and a treatment system was designed to remove soluble contaminants. However, permission was subsequently obtained to discharge effluent from both dewatering systems directly to the San Francisco sanitary sewer system. During initial operation, the air exhaust from the vacuum pump was scrubbed through a disposable activated carbon filter to remove volatile organics.

WASTE REMOVAL DURING FOUNDATION EXCAVATION

Excavation for the building basement was planned to extend to a maximum depth of approximately 20 feet below ground surface. This required removal of the overlying uncontaminated fill, the entire waste layer, and a portion of the underlying, slightly contaminated new bay mud. A soldier pile and lagging shoring system was utilized to prevent cave-in of the sidewalls during excavation.

The excavation process was complicated by the following factors:

- The need to minimize emissions of volatile and odor-producing hydrocarbons in order to protect the large population immediately surrounding the site

- The need for separate handling of the upper fill, waste layer, and underlying bay mud

- The requirement for excavation of the entire site up to a few feet from the fence line. This eliminated any potential buffer zone for dilution of potential air emissions, reduced the area available to stockpile soil, and required trucks to be staged on adjoining city streets.

The excavation plan was therefore designed 1) to reduce volatile emissions by minimizing the total exposed surface area of contaminated material at any given time and 2) to facilitate the separate handling of contaminated and uncontaminated soil by permitting only one type of material to be handled on a given day. Excavation began at the southern end of the site. A backhoe was used to remove uncontaminated overburden from a strip approximately 40 feet wide across the entire length of the site (on the east-west axis). Approximately 1 foot of clean overburden was left on top of the contaminated layer to prevent the release of volatiles and to provide a clean working area for the backhoe during the subsequent removal of contaminated material. The waste layer was excavated by a backhoe situated on the bench created by removal of the uncontaminated overburden. As the waste was excavated, it was placed in a pile on the bench directly behind the backhoe. A

second backhoe, located on the original ground surface above the first backhoe, removed the waste material from the stockpile and placed it directly into trucks. This process was repeated in increments from the southern end to the northern end of the site, with contaminated and uncontaminated material being hauled on alternate days.

The use of separate backhoes for excavation and loading allowed trucks to be loaded at a rate faster than the material was excavated, once a stockpile of sufficient size was created. This reduced truck standby time, an important consideration since the empty trucks had to be staged on city streets that were periodically clogged with rush-hour traffic.

Uncontaminated overburden was transported to a local debris fill. Approximately 3000 cubic yards of waste material was transported by a registered hazardous waste hauler to a permitted hazardous waste disposal facility. Following removal of the waste layer, the underlying bay mud was excavated and transported to a sanitary landfill. Due to the nonhazardous designation obtained for the bay mud, and the sequential excavation process which facilitated the separate handling of the three categories of materials, the expense of transportation by a hazardous waste hauler, and disposal at a hazardous waste facility was limited to the actual waste material.

HEALTH AND SAFETY CONSIDERATIONS

Because of the hazardous properties of the waste constituents and the large target population surrounding the site, health and safety considerations during the foundation excavation were of critical importance. A safety plan was developed which protected both construction workers and the surrounding community, while allowing construction activities to proceed without expensive delays. Close cooperation with state and federal regulatory agencies during the planning stage facilitated progress of the project once excavation began.

The primary volatile organic constituents of the waste layer--benzene, toluene, and xylenes--are acutely toxic in high concentrations. The link between chronic benzene exposure and leukemia and other blood disorders is also well documented (2). A few of the PNAs present in the waste layer are well documented animal carcinogens, including benzo(a)pyrene and benzo(b)fluoranthene (2). The primary health hazard associated with phenolic compounds, the third major class of constituents present in the waste material, is acute poisoning. All of these materials can be readily absorbed through the skin (2).

During safety plan development, three target populations were identified who could be affected by waste removal activities. The construction workers involved with excavation and installation of the shoring system would obviously have to work in close contact with the

waste. Based on their close proximity to the site during the entire excavation process, and the location of the buidling air intake above the excavation area, the occupants of the office building which bordered the site on two sides were identified as a second target population. The third target population consisted of users of adjacent streets and occupants of buildings farther removed from the site who would have a much lower potential for long-term exposure to release of airborne contaminants. A comprehensive health and safety plan was developed based on an analysis of applicable OSHA requirements for worker protection and Department of Health Services and EPA requirements for protection of the surrounding community.

The health and safety plan was comprised of the following major elements:

- Protecting construction workers by adopting standard safety procedures used at hazardous waste sites to the construction activities

- Protecting the surrounding community by preventing the emission of hazardous vapors and particulates

- Continuous air monitoring to evaluate the adequacy of respiratory protection for workers and the need to implement remedial actions to prevent off-site releases of contaminants

- Documentation of all monitoring results to limit future liability.

Air Monitoring Program

A comprehensive air monitoring program was established to address both worker and community safety. Fixed air monitoring stations containing an HNu photoionization detector (PI 101) with strip chart recorder, high-volume particulate sampler (Hi Vol), and sampling pump equipped with three-compartment sorbent tubes (silica gel, Tenex, and charcoal) were established at the northwest and southeast corners of the site. A similar station without the Hi Vol sampler was located at the air intake to the adjacent office building. The meteorological station was established across the street from the site. The location of the monitoring stations is shown in Figure 3.

Background values were measured for several days prior to the start of excavation. During excavation, monitoring was conducted along the entire fenceline and within the work areas using a hand-held photoionization detector (Photovac TIP). Because of the high toxicity and carcinogenic potential of benzene, rapid on-site identification of this constituent was of critical importance. This was accomplished by the periodic collection of grab samples in excavated glass globes and on-site analysis using a portable Photovac gas chromatograph equipped

with a photoionization detector. Breathing zone monitoring of construction workers was conducted using personal pumps equipped with charcoal tubes.

Worker Safety

Construction workers required to work in close proximity to the waste included heavy equipment operators, truck drivers, workers installing the lagging boards used to shore the sidewalls of the excavation, workers drilling and installing the tiebacks used to secure the shoring, grade checkers, laborers, carpenters, and supervisors. These workers were required to participate in a training program describing site-specific hazards and safety procedures, and were given comprehensive medical examinations before and after the waste removal.

All activities involving contact with waste were performed using Level C protection (Tyvek-Saranax coveralls, neoprene gloves and boots, latex undergloves and boot covers, twin-cartridge respirator with organic vapor cartridges, hard hat, and face shield). The entire site was designated as an exclusion zone, with a decontamination line and portable trailer containing showers and lockers located at the northwest corner.

Total hydrocarbon concentrations were measured in the work area during excavation using a Photovac TIP. When concentrations in the breathing zone area approached 0.4 ppm (benzene equivalent), a grab sample was collected and immediately analyzed for benzene. Benzene was never detected in on-site analyses at levels greater than the detection limit of 0.1 ppm. The highest 8-hour time weighted average values measured in the workers' breathing zone using charcoal tubes were 0.15 ppm benzene, 0.18 ppm toluene, and 0.07 ppm xylene. The benzene value is approximately 65 times less than the threshold limit value of 10 ppm. These were obtained in a work area where lagging boards were being installed directly against the exposed waste.

Community Safety

The primary hazard to the surrounding community was the potential release of volatile constituents during waste excavation. Evaluation of potential hazards from airborne particulates indicated that such releases would be unlikely because all waste and contaminated soil was located below the water table. The relatively small size of the site, although a disadvantage in almost all other respects, facilitated site entry control; this was achieved with chain link and plywood fencing and the use of security guards. Because excavation would take place almost to the fenceline, sidewalks fronting the site were closed and pedestrian traffic redirected to the opposite sides of the streets.

Vapor suppression contingency plans were developed to ensure that excavation could proceed without endangering the surrounding community.

If specific action levels for total hydrocarbons, benzene, toluene, and xylene were exceeded at the fenceline or the air intake to the 215 Fremont Street Building, the following vapor suppression measures would be taken:

- The exposed working face of contaminated soil in the excavation area would be covered with plastic sheets or clean soil, except in the immediate area where the backhoe was working.

- If significant vapor reduction was not achieved, a temporary fluorocarbon vapor-suppression foam (FX-9160, manufactured by 3-M Corporation) would be applied to the active working face; contaminated soil in the backhoe buckets, stockpile of contaminated soil awaiting loading, and contaminated soil in truck beds during loading.

- If significant vapor reduction was still not achieved, excavation would be stopped and all exposed waste covered.

Action levels that would trigger the vapor suppression measures are shown in Table 3. Because occupants of the adjacent building would potentially be exposed to any volatile emissions from the excavation for the duration of the project, significantly lower action levels were set for the building air intake. Prior to the start of excavation, the air intake was rerouted so it would not draw air from directly above the project site, and windows facing the excavation were sealed to prevent air intake.

Although total hydrocarbon concentrations up to 40 ppm were measured directly above newly-exposed waste during excavation, the action level of 0.5 ppm total hydrocarbons was never exceeded at the fence line or the air intake. Excavation was able to proceed without implementing the vapor suppression contingency plan.

BUILDING WATERPROOFING

Because the basement would extend up to 10 feet below the water table, the building was designed with a passive waterproofing system. The original system utilized a mastic, which was found to be subject to degradation by the waste constituents. Because the waste deposit under the adjacent building and city streets would remain in contact with the foundation, bentonite panels resistant to degradation by the waste were substituted.

PROJECT TIMELINE

The waste deposit was first discovered in early February 1985. By March 31, 1985, a remedial action plan describing the nature and extent of contamination, excavation procedures, and worker and community safety considerations was approved by state and federal regulatory

Table 3. Action Levels for Implementing Vapor Suppression Contingency Plan

Monitoring Location	Level (measured value minus background)	Action Taken
Site perimeter	0.5 ppm total hydrocarbons	Collect grab sample for GC analysis
	0.5 ppm benzene, 25 ppm toluene/ xylene	Surface control - plastic
	0.5 ppm benzene, 25 ppm toluene/ xylene after plastic applied	Surface control - foam
	0.5 ppm benzene, 25 ppm toluene/ xylene after foam applied	Stop work - cover exposed waste
Air intake - Adjacent building	0.5 ppm total hydrocarbons	Implement surface controls in order listed above

agencies. Excavation of the waste deposit began on May 16, 1985 and was completed on June 16, 1985, less than six months after initial discovery.

CONCLUSIONS

Although all of the coal tar waste present within the site was removed, this material probably extends throughout the area built on the western portion of Yerba Buena Cove. The City and County of San Francisco should take an active role in notifying affected property owners of the existence of this deposit so that waste removal is included in planning for excavations within this area.

Hazardous waste problems are usually attributable to modern society's increasing reliance on chemical technology to provide a high standard of living. In this case, a significant hazardous waste problem was created in an era usually thought to predate environmental pollution, and this waste lay dormant for 120 years before its discovery. As is the case with most hazardous waste problems, simply covering the waste at the Tar Flats with earth merely handed the problem down to a later generation.

ACKNOWLEDGMENTS

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SAN FRANCISCO
SHORELINE 1853

SAN FRANCISCO
SHORELINE 1859

SAN FRANCISCO
SHORELINE 1869

Figure 1
Sequence of filling in
Yerba Buena Cove

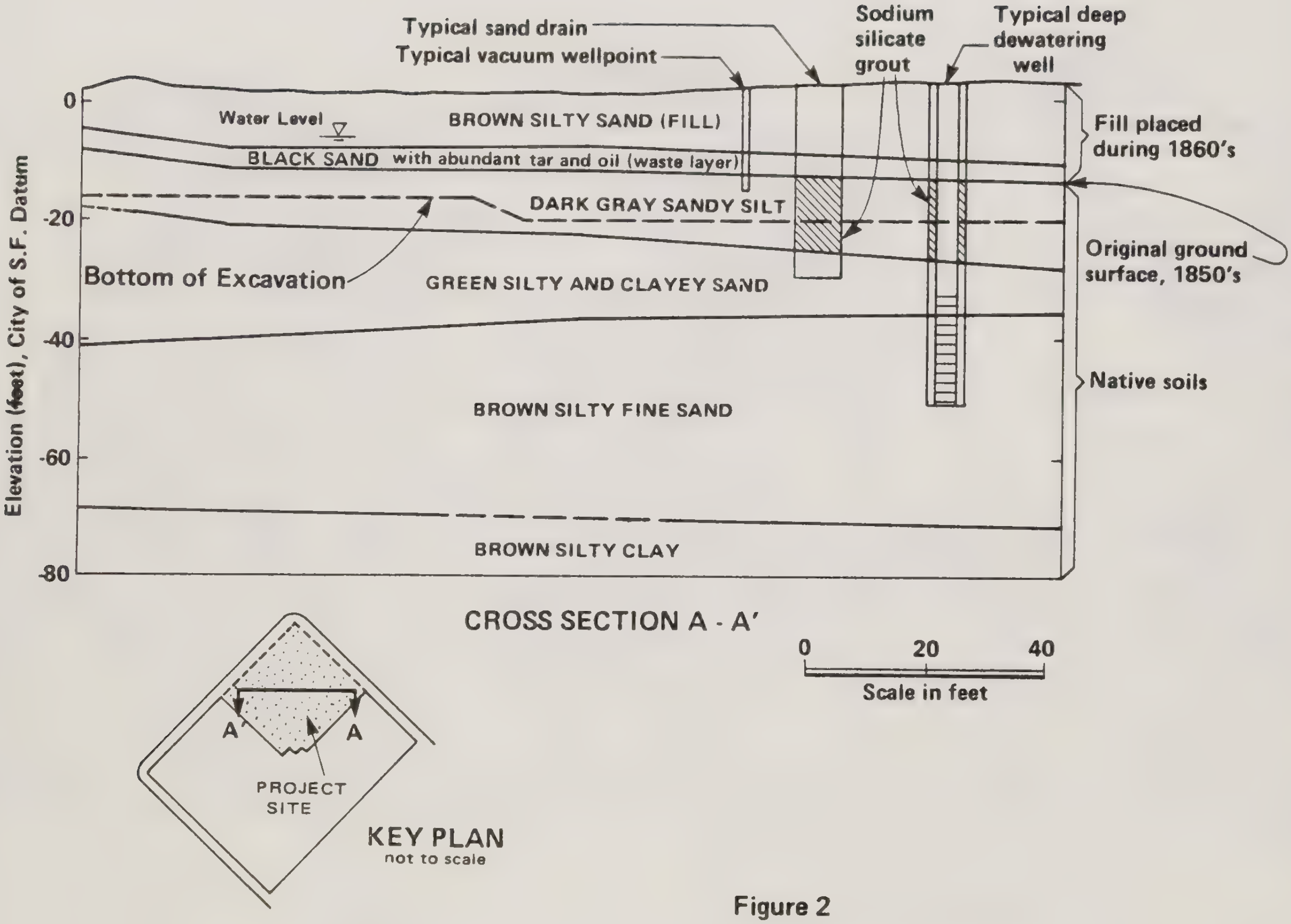

Figure 2
Subsurface soil conditions and typical dewatering wells

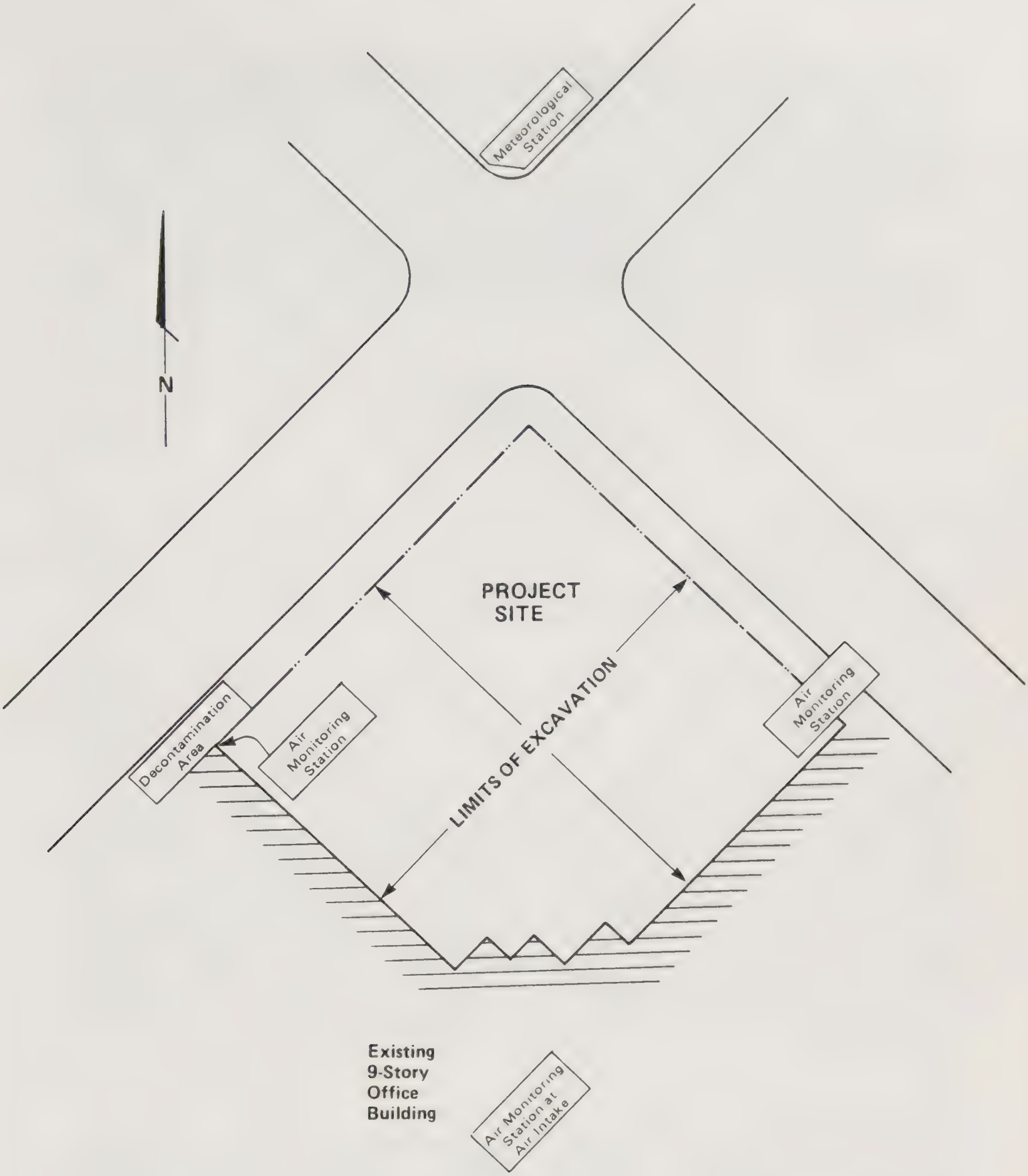

Figure 3
Site Plan

EMERGENCY RESPONSE TO A UNIQUE ASBESTOS PROBLEM

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INTRODUCTION AND DEFINITION OF ASBESTOS

Because of the variety of organizations involved in asbestos mining industry and regulations, such as mineralogists, attorneys, industrial users, economists, and occupational health agents, "asbestos" has become a generic and often misinterpreted term. The Occupational Safety and Health Administrations (OSHA) has defined asbestos as any fibrous material containing a length to width ratio of at least three to one and having a length of at least five microns and a maximum diameter of not greater than five microns. Despite the fact that some asbestos fibers in mineral deposits are tens of centimeters long (Ross 1981), the majority of fibers are considerably shorter (Figure 1). Geologically, asbestos falls into two mineralogical categories: the serpentine and the amphibole group. Chrysotile, which comprises the overwhelming majority of commercially mined asbestos (95%), is a form of serpentine. The only commercially exploited mineral within the amphibole group is crocidolite. All of the other fibrous amphiobole minerals are rare and, except for a few isolated economic deposits, are not commercially important (Figure 2) (Ross 1981). These include amosite, anthophyllite, actinolite, and tremolite.

GEOLOGIC OCCURANCE OF ASBESTOS

Serpentine deposits containing asbestos, particularly ones that are commercially exploitable, are found largely in areas of igneous intrusive activity with closely associated metamorphism or in areas with tectonically emplaced ophiolites. In North America, such geologic settings occur on both the east and west coasts. Several localities within the Appalachian Mountains in Georgia, North Carolina, Maryland, and Massachusetts have yielded significant amounts of amphibole asbestos. The northern extent of the Appalachian Mountains in Southeastern Quebec and Northern Vermont are among the most important chrysotile producing areas in the North American mountain chain. An active asbestos mine is still located in Hyde Park, Vermont (US EPA Doc #530-SW-85-007).

In a similar geologic setting, relatively large deposits of chrysotile asbestos are found in California, most commonly along the contact of two distinct groups of predominantly sedimentary rocks: The Franciscan Formation and Great Valley Sequence (Bailey, Irwin, and Jones, 1964) (Figure 3). East of the Great Valley in the foothills of the Sierra Nevada Range, small pods of chrysotile-containing serpentine occur along northwest trending faults within chiefly volcanic and metamorphosed volcanic rocks. Currently, there are two active mines located in California, one in Santa Rita about 15 miles north of Salinas, and the other in the small community of Copperopolis in the Sierra Nevada Foothills (Figure 3). Two other mined areas in California were closed in the 1970's due to environmental controls and fiber shortness. One of the localities is in Coalinga which may have reserves of up to tens of millions of tons of 50 percent chrysotile (typical grades of asbestos range from one to five percent) (Ross, 1981).

CONSUMPTION

As a result of being heat resistant, resistant to corrosion, having a high tensile strength and a low conductivity, and being easily woven into fibers, asbestos has been employed in a number of different products (Table 1). The most popular uses of asbestos include cement pipes, flooring products, friction materials, asbestos cement sheets, coatings and compounds, paper, packing materials, and insulation (Pierce and Garcia, 1983).

TOXICITY

DISEASE

There are three respiratory diseases associated with the inhalation of asbestos fibers: 1) Lung cancer, 2) Asbestosis, a fibrosis of the lung tissue which reduces the elasticity of the lung and its functions, and 3) Mesothelioma, a rare but fatal cancer of the plueral and peritoneal membranes. Although several studies have linked asbestos exposure to a higher rate of lung cancer in cigarette smokers, no relationship is evident between smoking habits and mesothelioma or asbestosis. Additionally, an increased risk of lung cancer attributable to asbestos exposure in non-smokers appears low. In all three respiratory diseases symptoms generally do not appear for at least 20 years.

EFFECTS OF PARTICLE SIZE

Whether asbestos fibers enter the lung or penetrate the small bronchioles and alveolar sacs appears to be determined by fiber size and shape (Ross 1981). Particles having diameters less than five microns can effectively enter the lung and bronchioles and alveolar sacs while those with diameters greater than five microns cannot. Most fibers entering the upper respiratory tract are removed by a system of mucous membranes and cilia. Particles in the lower respiratory tract are removed by macro phages which engulf the particles and either transport them to the upper respiratory tract for expulsion or move them through the alveolar wall and ultimately to the lymph channels. However, it is thought that fibers longer than five microns may remain in the lower respiratory tract and cause the tissue to become fibrous thereby forming the beginning of asbestosis.

ASBESTOS REGULATORY PROGRAMS

Asbestos is listed as a hazardous air pollutant in the Clean Air Act (CAA) and as a toxic pollutant in the Federal Water Pollution Control Act (FWPCA). Airborne asbestos is regulated by the National Emissions Standards for Hazardous Air Pollutants (NESHAPS). OSHA is responsible for regulating asbestos in workplaces while the US EPA's Toxic Substance Control Act (TSCA) regulates asbestos in schools. Because its disease causing properties meet the criteria established in the statutory definition of RCRA (although asbestos is not listed as a hazardous waste under RCRA) and its listing in the CAA and FWPCA, asbestos is a hazardous waste under CERCLA. This enables the EPA to take emergency and/or remedial action to mitigate an imminent and substantial threat to the environment or to public health.

CASE HISTORY OF ALVISO, CA

SITE BACKGROUND

The community of Alviso, population 1700, is located at the southern tip of the San Francisco Bay, northeast of the Guadelupe River and south of the Alviso Sloughs (Figures 4 and 5). Waste asbestos in the form of sludges, asbestos pipes, siding, and insulation have been generated by several sources since the 1950's. This waste has been used as landfill to elevate property to buildable heights since the community lies below sea level (Figure 5). Asbestos pipes were also used to drain excess water from property and to drain septic tanks onto gravel roads. The total volume of asbestos waste deposited in dump sites at Alviso since the 1950's is estimated to be 40,000 cubic yards.

During 1963 and 1964, the Santa Clara Valley Water District (SCVWD), in conjunction with the U.S. Army Corp of Engineers, straightened the Guadelupe River to minimize flooding damage in Alviso. While straightening the river, dump sites containing waste asbestos materials were uncovered on land belonging to the SCVWD and the City of San Jose. Additionally, in 1983, a six-foot ring levee was built around the town to aid the efforts to prevent flooding damage. This ring levee has also been identified as being a potential significant source of asbestos within the community, as high levels of chrysotile asbestos have been found within its soil matrix. The Guadelupe River still floods frequently, most recently during the winter of 1983, spreading asbestos throughout the town. Preliminary results from soil sampling from the Department of Health Services Air and Industrial Hygiene Laboratory indicated asbestos concentrations between 20 and 40 percent (by weight).

EPA INVOLVEMENT

Further soil sampling by the California Department of Health Services (DOHS) documented asbestos concentrations from 0.01 to five percent. Airborne sampling revealed inconclusive results. At this point, because of the suspected extent of the problem and the probable cost involved in its mitigation, the U.S. Environmental Protection Agency's Emergency Response Section was requested to investigate the problem and pursue corrective measures.

SAMPLING

Since the major health concern considered with asbestos is the inhalation of fibers, initial soil sampling was focused on unpaved roads where vehicle traffic would generate clouds of dust potentially contaminated with asbestos. Areas fitting these descriptions included a one-half mile section of Spreckles Avenue, a parking lot behind the George Mayne Elementary School, and the O'Niel Tract, a small development adjacent to the school. Soil samples were also gathered from the ring levee which was suspected to be a source of asbestos. Material to build this levee was imported from a nearby quarry which contains significant amounts of serpentine.

LABORATORY ANALYSIS

SELECTED ANALYTICAL TECHNIQUES FOR ALVISO SAMPLES

All of the soil samples gathered were analyzed for asbestos using polarized light microscopy (PLM). PLM was chosen because of the benefits of relatively low cost, rapid turn-around time, and the desired detection limit of one percent. Results are reported in volume percent and are semiquantitative. Air samples were collected on a cellulose filter and analyzed using a phasecontrast microscope at 400-450x magnification. A detection limit of .001 fibers/cc was achieved as roughly 4800 liters (10 l/mm, 8 hour time limit) of air was drawn through the filter.

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

In order to ensure the quality of the data, several precautions were followed in the field and by the contracted laboratory. One blind blank was submitted for every tenth air sample gathered. In addition, blind duplicates were also submitted during the remedial sampling.

To ensure accurate quantification of asbestos, bulk (ie. soil) samples are examined for homogeneity and preliminary fiber identification at low magnification. Following fiber identification, quantification is performed using the point counting method. This involves counting the fibers in one section of the slide and extrapolating that figure to include the entire area occupied by the slide. Internal QA/QC is accomplished by reanalyzing every tenth sample. This type of analysis can be quite objective and results can vary from operator to operator. With the analysis done for this project only one operator performed all the analysis. The estimation of precision and accuracy of results is made difficult due to this nature of analysis. Similarly, internal QA/QC is performed on air samples submitted for asbestos analysis by the lab. Any sample results which do not satisfy the counting repeatability at the 95% confidence level are discarded.

RESULTS

Results of the soil sampling are shown in Table 2. Of the 35 samples taken on Spreckles Avenue 57 percent (20 samples) contained asbestos concentrations greater than the one percent detection limit. Fifty percent (six samples) of those gathered at the elementary school revealed similar concentrations. Only one sample (1.5 percent) of those taken from

the O'Niel Tract contained a concentration of at least one percent. Seventy-six percent (13 of 17 samples) from the levee showed concentrations above one percent. One sample contained asbestos contents of 15 percent (Figure 6).

DISPOSAL ALTERNATIVES FOR ASBESTOS

According to the EPA the only option acceptable for the permanent disposal of asbestos is burial. This can be accomplished by one of three methods: 1) Excavation and transportation to an off-site landfill, 2) Burial in an on-site landfill, and 3) Insitu capping. The considerations important in choosing an alternative at Alviso included the extent and volume of contaminated soil, topography, climate, future use, number of inhabitants, and cost. The volume of contaminated soil in Alviso was estimated to be roughly 2000 m3 (excavating Spreckles Avenue and the parking lot at the elementary school to an arbitarily chosen four inch dept). Considering transportation and disposal costs for such a large volume obviously excluded alternatives one and two. These same alternatives were also ruled out by the fact that nearly 2000 people live in Alviso. Excavation of 2000 m3 of soil would cause a major disruption in the everyday lives of the inhabitants in addition to generating large volumes of asbestosladen dust. Since Alviso already lies below sea level, excavation and either on-site or off-site burial seemed impractical. This, combined with the generally dry climate (and therefore a lack of ability to trap dust), suggested that the only economical and sensible option was in-situ capping (ie. paving). This not only would solve the problem of dust generation but also provide the community with a new paved road.

EMERGENCY RESPONSE ACTION

The two areas of greatest concern in Alviso were a heavily travelled half-mile unpaved stretch of Spreckles Avenue and an unpaved parking lot behing the George Mayne Elementary School and the O'Neil Tract. Because these areas were unpaved, large amount of asbestos-contaminated dust were generated from vehicle traffic. The O'Neil Tract roads did not require any stabilization due to the absence of asbestos above the action level of one percent. Insitu capping (paving) was selected to alleviate the problem for the aforementioned reasons.

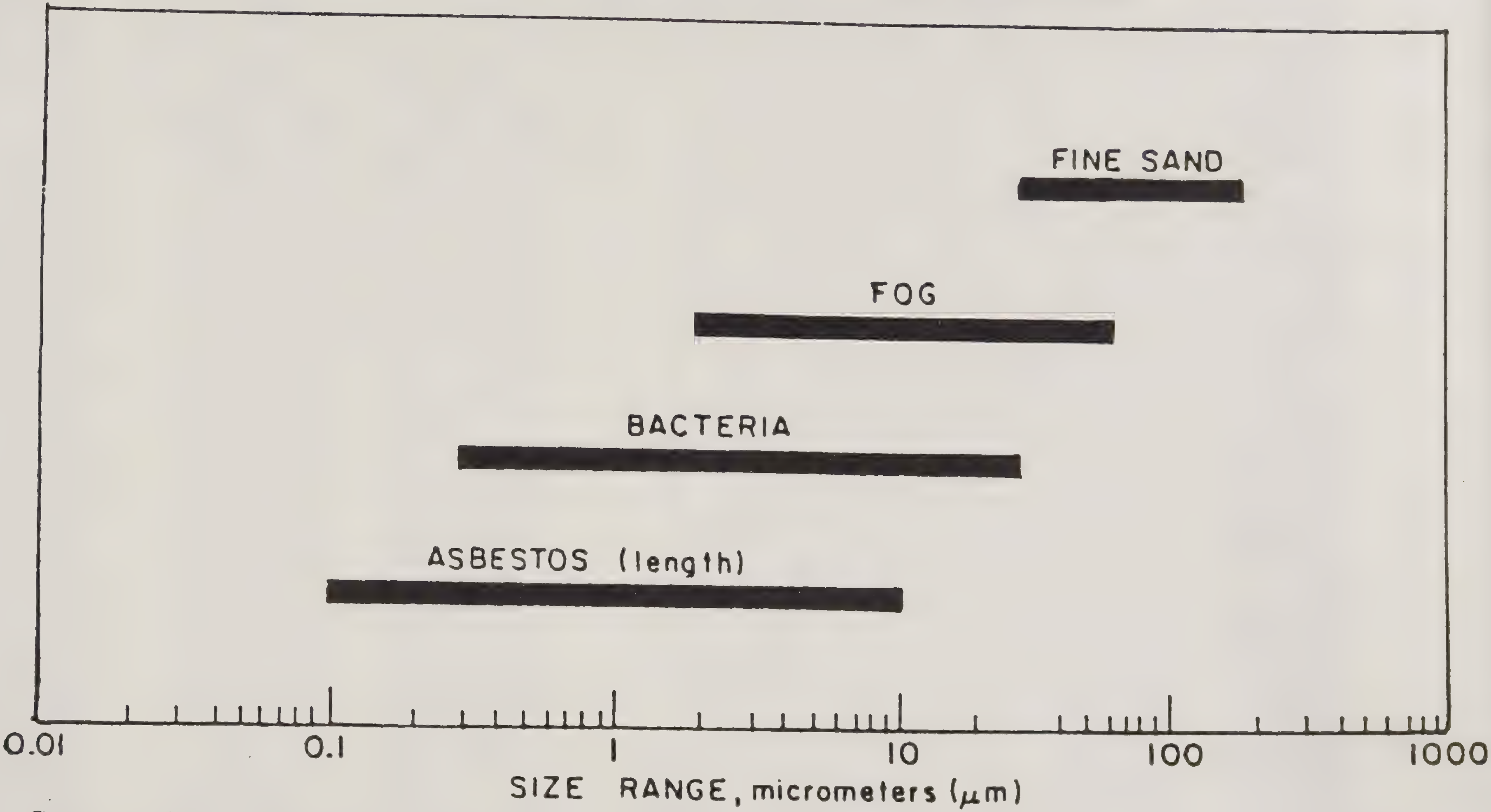
Air monitoring was conducted before, during, and after the paving to document the concentrations of generated airborne asbestos. Sampling times during the paving were eight hours (at 11 liters per minute) while five hour periods (also at 11 liters per minute) were used after the paving. As can be seen from Table 4 no detectable airborne fibers were generated before, during, or after the paving activities.

CONCLUSIONS

After considering the history and potential significant asbestos contamination at Alviso, a preliminary assessment was conducted by the EPA. This survey revealed asbestos concentrations of up to 20 percent on one heavily travelled dirt road and school parking lot. Further soil sampling of unpaved roads indicated that only the school parking lot and Spreckles Avenue contained asbestos concentrations greater than the

Emergency Response Section action level of one percent. After considering several alternatives it was decided that capping (paving) these areas was the most economical and feasible way to minimize public exposure to airborne asbestos fibers. Concurrent air monitoring showed that no airborne fibers were generated before, during, or after the grading and paving.

Figure 1. Asbestos size comparison with other particles.



Source: EPA 450/2-78-014, March 1978.

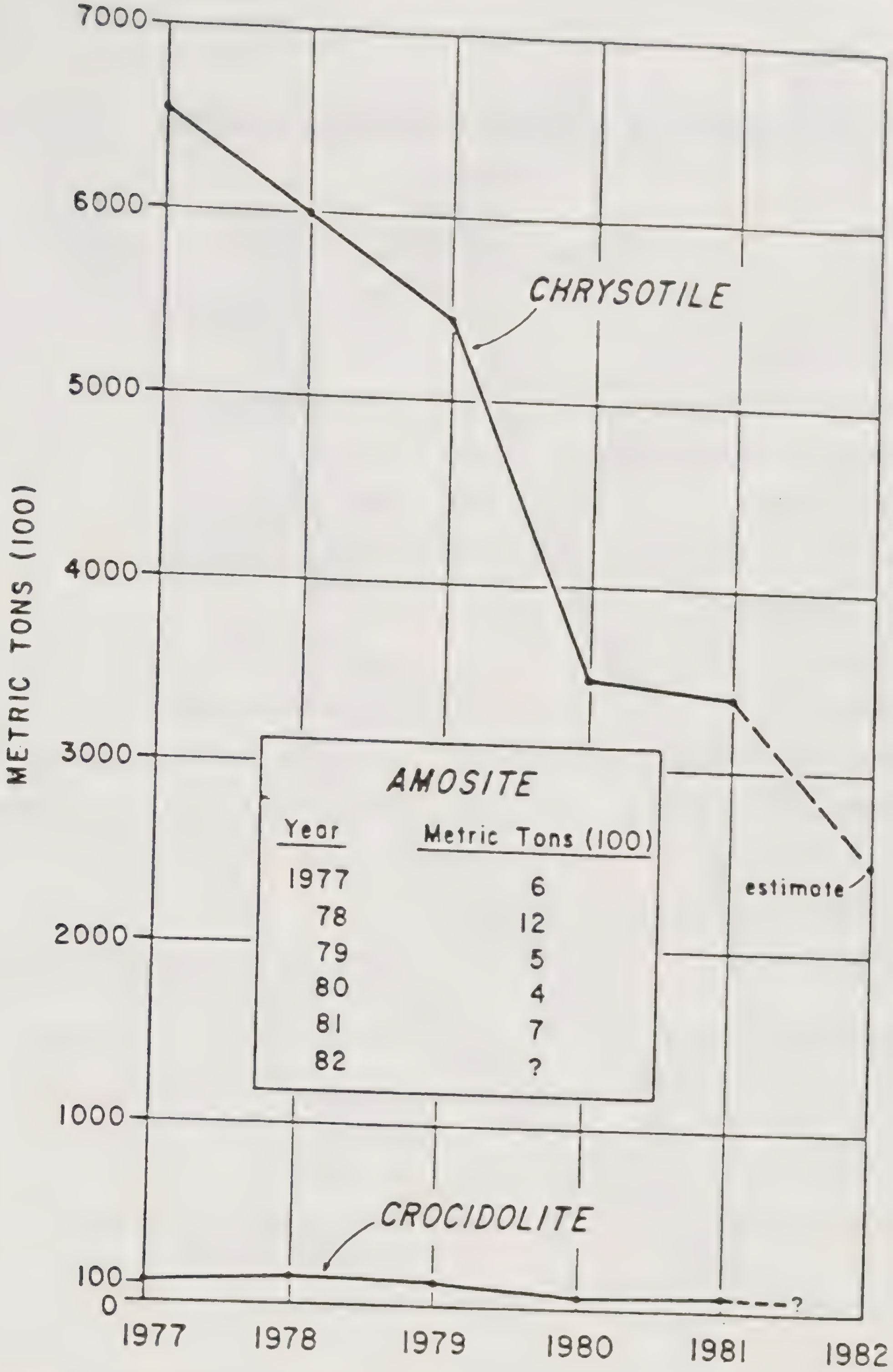


Figure 2 U.S. asbestos consumption by fiber type (100 metric tons), 1977-1982.

Table 1. Summary of Asbestos-Containing Products

Product	Average percent asbestos	Binder	Dates used
Friction products	50	Various polymers	1910-present
Plastic products			
Floor tile and sheet	20	PVC, asphalt	1950-present
Coatings and sealants	10	Asphalt	1900-present
Rigid plastics	<50	Phenolic resin	?-present
Cement pipe and sheet	20	Portland cement	1930-present
Paper products			
Roofing felt	15	Asphalt	1910-present
Gaskets	80	Various polymers	?-present
Corrugated paper pipe wrap	80	Starches, sodium silicate	1910-present
Other paper	80	Polymers, starches, silicates	1910-present
Textile products	90	Cotton, wool	1910-present
Insulating and decorative products			
Sprayed coating	50	Portland cement, silicates, organic binders	1935-1978
Trowelled coating	70	Portland cement, silicates	1935-1978
Preformed pipe wrap	50	Magnesium carbonate, calcium silicate	1926-1975
Insulation board	30	Silicates	Unknown
Boiler insulation	10	Magnesium carbonate, calcium silicate	1890-1978
Other uses	<50	Many types	1900-present

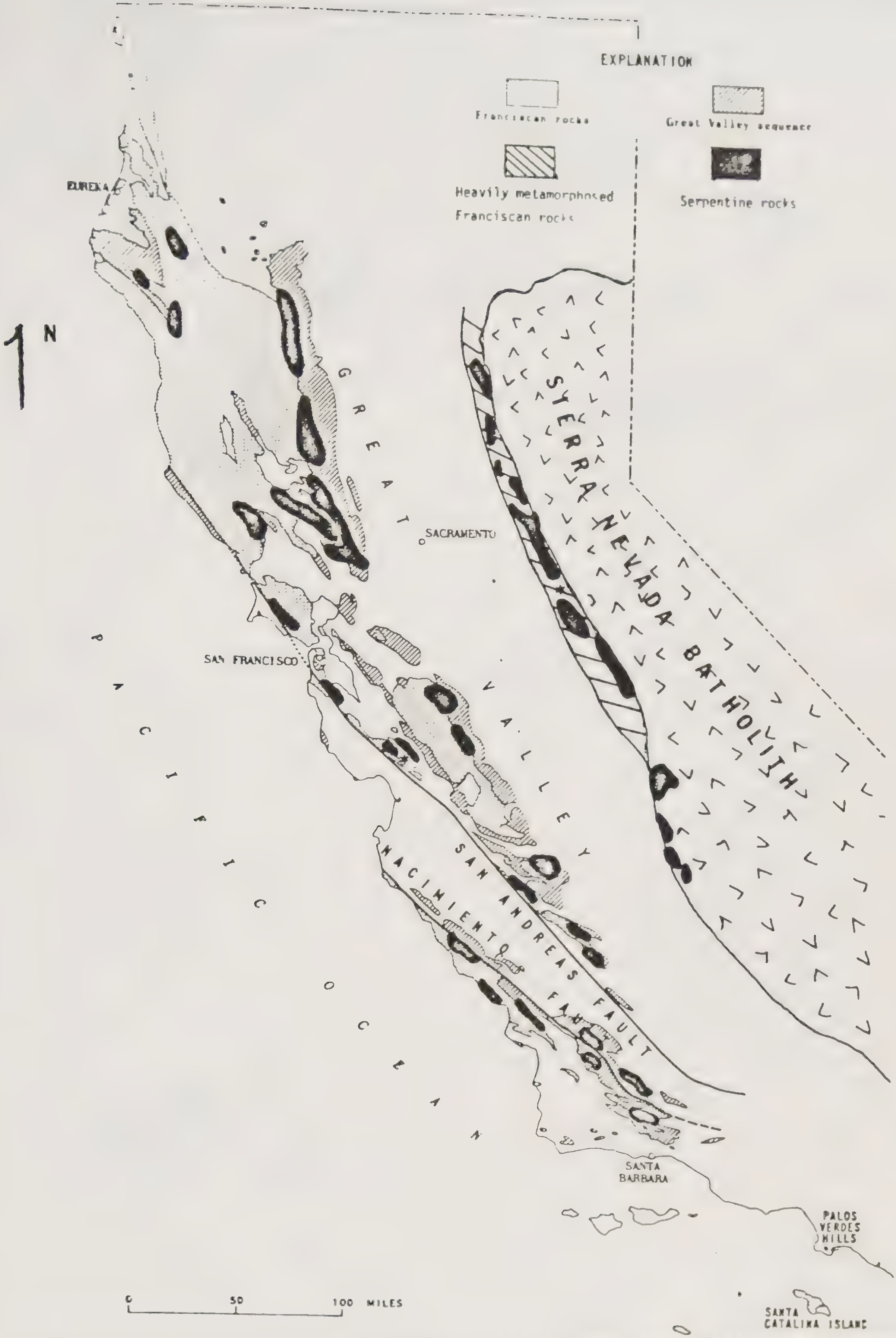


Figure 3 - Geologic map of California illustrating the relationship between the Franciscan Formation, Great Valley Sequence. and serpentine deposits. The Santa Rita Mine (Western California) and the Copperopolis Mine (Sierra Foothills) are denoted by stars. See text for discussion.

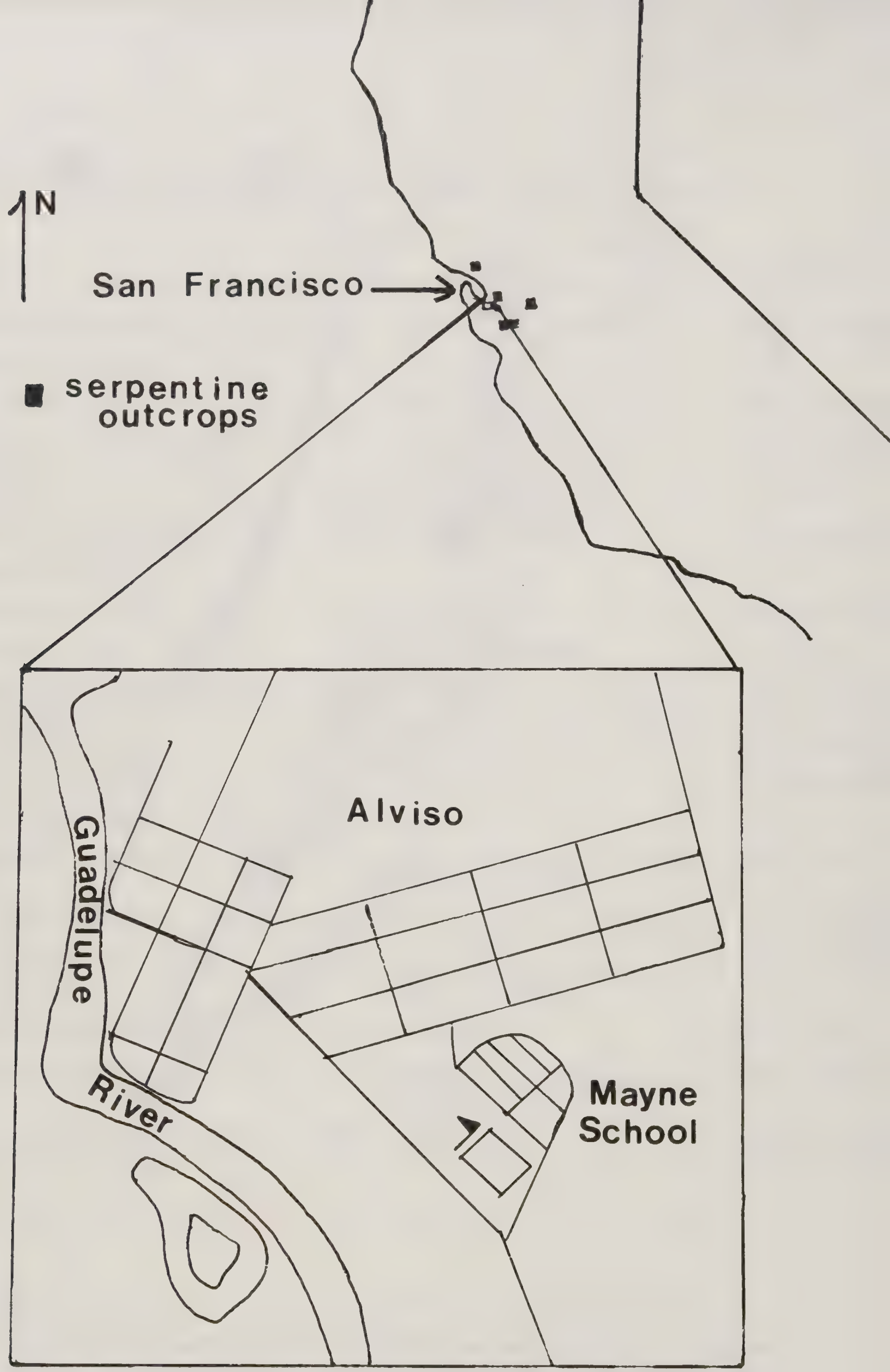


Figure 4 - Location of Alviso
Note the proximity to serpentine outcrops.

Figure 5 - Detailed map of Alviso.
Dashed and hatched lines indicate levees.
The entire community resides about four feet below sea level

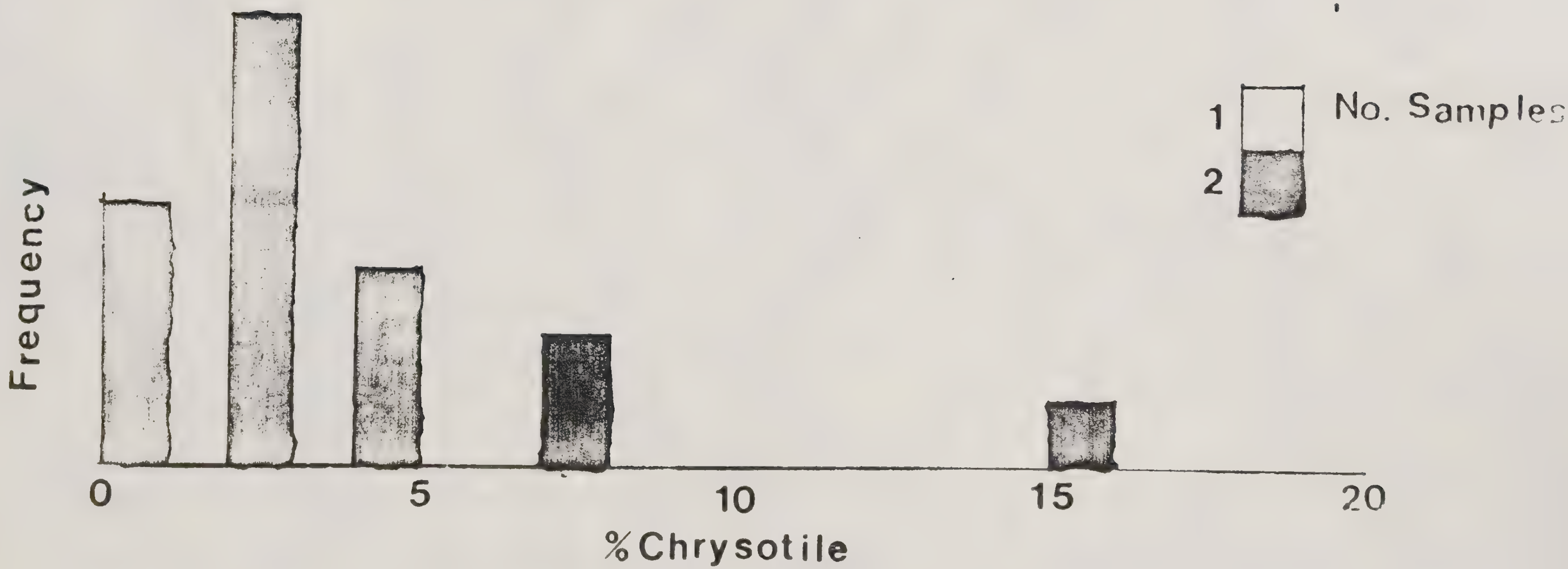


Figure 6 - Transmitted light microscopy results from the ring levee.

Table 2 - Transmitted light microscopy results from surface soil samples Numbers 1-35 are from Spreckles Avenue, 36-47 are from the elementary school

Sample No.	Percent Chyrsotile	Sample No.	Percent Chyrsotile
1	3-5	25	<1
2	1-3	26	<1
3	1-3	27	<1
4	1-3	28	1-3
5	1-3	29	1-3
6	1-3	30	<1
7	<1	31	<1
8	<1	32	<1
9	1-3	33	<1
10	1-3	34	1-3
11	1-3	35	<1
12	3-5	36	<1
13	1-3	37	<1
14	1-3	38	1-3
15	<1	39	3-5
16	1-3	40	3-5
17	<1	41	1-3
18	<1	42	1-3
19	<1	43	<1
20	1-3	44	<1
21	1-3	45	<1
22	<1	46	1-3
23	1-3	47	<1
24	1-3		

Table 3 - Transmitted light microscopy results from the O'Niel Tract.

Sample No.	Percent Chyrsotile	Sample No.	Percent Chyrsotile
1	1-2	35	trace
2	trace*	36	N/D
3	trace	37	trace
4	trace	38	trace
5	trace	39	trace
6	trace	40	trace
7	trace	41	N/D
8	N/D+	42	trace
9	trace	43	trace
10	trace	44	N/D
11	trace	45	N/D
12	trace	46	trace
13	trace	47	N/D
14	trace	48	trace
15	trace	49	trace
16	trace	50	trace
17	trace	51	trace
18	N/D	52	trace
19	trace	53	trace
20	trace	54	trace
21	trace	55	trace
22	trace	56	trace
23	trace	57	trace
24	trace	58	trace
25	trace	59	trace
26	trace	60	trace
27	trace	61	trace
28	trace	62	trace
29	trace	63	trace
30	trace	64	trace
31	trace	65	trace
32	trace	66	trace
33	trace	67	trace
34	trace		

*Trace - one percent (detection limit)

+N/D - no chrysotile detected (one percent detection limit)

Table 4. Results of air monitoring before, during, and after the grating and paving of the dirt roads.

Sample No.	Percent Chrysotile
1-10	Before: N/D+
1-10	During: N/D
1-4	After: N/D (Samples from school only)

+: no chrysotile detected (detection limit of one percent)

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THE INVESTIGATION AND CLEANUP OF PESTICIDES IN SOIL AND GROUNDWATER

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INTRODUCTION

Past design and operating practices in the manufacture, formulation, distribution, use, and disposal of pesticides has lead to elevated levels of pesticides in the soil and groundwater at several hundred sites in California. Regulatory programs being implemented by the California Regional Water Quality Control Boards (RWQCBs) and California Department of Health Services have identified many of the sites for investigation and cleanup. This paper will present an overview for investigation and cleanup of soils and groundwater associated with sites where many different types of pesticides have been released in soil and groundwater. At the Hazmacon Conference, several site investigation and cleanup projects will be presented that illustrate the principle summarized in this paper.

The concern of the public and regulatory agencies in the investigation and cleanup of these sites should ultimately be the risks to human health and environmental health resulting from the pesticides in the soil and groundwater at the site. The risks, consequently the need for cleanup, depend on the potential routes of exposure and the toxicity of the pesticides to which humans or the environment are exposed. The technical feasibility of remedial measure will depend on the benefits and risks associated with cleanup technology to reduce the risks of exposure to acceptable levels in the most cost-effective manner. In the investigation and cleanup of sites with pesticides in soil and groundwater, the chemical as well as the physical nature of the environment and pesticides must be considered.

SITE INVESTIGATION

The purpose of a site investigation is to characterize by the risks associated with pesticides in soil and groundwater, and provide technical information for the development of cleanup plans if necessary. The assessment of the risks associated with pesticides in the soil and groundwater are generally approached by determining:

1. What concentrations of the chemical are in soil and groundwater,

2. How the pesticides travel through the environment,

3. How the pesticides are transformed in the environment to form other chemicals, and

4. What human and environmental exposure results from the pesticides and breakdown products.

Site specific investigation plans to characterize the risk associated with various pathways potentially causing human and environmental exposure are developed through the determination of the following site specific information:

- The mechanism of release of the pesticides;

- The types and toxicity of pesticides released to the soil and groundwater;

- The fate and mobility of the pesticides; and

- The potential exposure of the public, and the organisms to the soil and groundwater containing the pesticides or breakdown products.

In most cases where pesticides have been released to the environment from usage and disposal, the primary pathways of exposure are direct contact with soil and sediments containing the pesticides, and contamination of the groundwater used as drinking water supplies. The cleanup of these sites generally entails the removal or placing of a cap over the soils and sediments with the highest concentrations. In a few cases where groundwater contamination exists, systems have been installed to contain and treat the groundwater with elevated levels of the pesticides and solvents. In very few cases alternative drinking water

supplies have been provided for people who use the groundwater with elevated levels of pesticides for drinking water supplies. The factors affecting the risks and need for remediation at sites with elevated levels of pesticides in the soil and groundwater are briefly described below.

Mechanism of Release

In most instances, the pesticides are spilled directly onto the ground or released to soils and sediments as aqueous solutions produced from washing of equipment or facilities. Frequently, elevated levels of pesticides in the soil and groundwater have been caused by the use of unlined evaporation ponds for the disposal of the wastewater from the manufacture, formulation, and use of the pesticides. Elevated levels of pesticides are being found at sites such as drainage ditches of a few feet wide and less than two hundred feet long to several acres and surface impoundments.

Types of Toxicity of Pesticides

Many types of insecticides and other pesticides have been disposed of over the thirty or more years at many of the sites. Each site appears to have a unique set of pesticides that have been disposed at the site. At sites where pesticides have been mixed and application equipment have washed over several decades, thirty or more organochlorine, organophosphates, and urea based pesticides, as well as solvents, may have been released to the soil and groundwater. The procedures are expensive for analyzing those pesticides that have developed analytical procedures. The cost for a single soil sample can range from several hundred dollars to over two thousand. For several of the pesticides, EPA test methods do not exist, than requiring extensive and costly laboratory test procedure development.

If all of the pesticides are tested for in each of the soil samples needed to assess the extent of soil contamination at a site covering even a few hundred square feet around a mixing and cleaning area, it can be very expensive. Therefore, in developing the sampling plan, it is important to select specific pesticides or group of pesticides to be analyzed for as indicators for the presence of other pesticides. As part of the initial soil and groundwater sampling at a site, the use of indicator parameters for the rest of the testing program should be verified. Use of these parameters save substantial resources for the

completion of subsequent testing for definition of the extent of contamination at a site. In selecting the indicator parameters, the toxicity of the pesticides and the fate and mobility of the pesticides must be considered.

Hydrogeology of the Site

The hydrogeology of each site differs and must be characterized so that the risks from the exposure of the pesticides and transformation products in the groundwater and surface water can be assessed. The major hydrological features affecting the transport of the pesticide in soil are the surface recharge and runoff that can cause the pesticides to move through the environment. The depth to groundwater and the interconnection of the upper groundwater aquifers to the lower aquifer used as drinking water supplies are the key environmental factors that should be defined during the site investigation studies.

Generally the staff of the RWQCBs require that the potential for transport of the pesticides from upper aquifers to lower aquifers used for drinking water to be defined during the site investigation studies. Abandoned wells and wells that are completed in multiple zones can be important conduits for movement of pesticides from the upper aquifers to the lower aquifers.

The extent of and concentration of pesticides which are in the unsaturated zone below the surface spills and impoundments and above the groundwater should also be well defined. Knowing the types and levels of pesticides in the unsaturated zone is a key factor in assessing the future risks associated with the release of pesticides to the environment. The staff of the Regional Water Quality Control Boards generally require that one soil boring drilled to the groundwater at sites with small areas of shallow soil contamination in drainage ditches. Soil samples should be collected from the soil boring and analyzed for pesticides in order to develop a vertical concentration profile. The boring is usually then completed as a groundwater monitoring well for the site. From the data on the porosity and permeability of the soils and elevation of groundwaters, the flow of water through the unsaturated and saturated zones can be characterized.

Fate and Mobility

The fate and mobility of chemicals in an environmental system are functions of the properties and reactivities of the chemical and the properties of the system (called environmental variables). Some environmental variables are evaluated by hydrogeological methods that determine important information such as the porosity and permeability of soils in the unsaturated and saturated regions, and the groundwater flow rate and direction. The hydrogeology of the area is then one important factor needed to determine the pathways by which chemicals may move at the site, but not the only factor to be considered. As part of the studies to characterize a particular environment, soil and groundwater properties such as pH and percent organic content also need to be measured.

The evaluation of the reactivity of a chemical is also important, among other reasons, to explain why some chemicals persist at site whereas others are no longer present (i.e., they have been transformed to products, which may be of concern themselves.) While biological processes (involving bacteria, fungi, or other organisms) are probably responsible for transforming many chemicals that enter the environment, the complexity of the biological processes themselves do not allow any reliable prediction of the rates of these processes in the natural environment. There is, however, a large amount of literature that can be used to evaluate qualitatively the conditions and the ease under which certain groups of pesticides may undergo biotransformation reactions, and also what products may be expected under these conditions.

Of the various biological and chemical processes that may occur in soil/water systems, chemical hydrolysis is most amenable to predicting reliable transformation rates. While the other processes may be more rapid in some environments, for many chemicals the simple dependence of hydrolysis reaction rates on pH only allows for reliable estimates of maximum half-lives of some pesticides dissolved in water.

Risk Assessment

Once the extent and movement of the pesticides and breakdown products are defined, the risks associated with exposure to the pesticides should be characterized for each major pathway. The need for cleanup of the soil and

groundwater to reduce the risks to an acceptable level should be determined on the basis of the risks to humans and the environment, the regulatory requirements, the concerns of the community, the long term liabilities to the site owner associated with release of the pesticides, and the current and future land use of the site.

SITE CLEANUP

The development of plans for the cleanup of the site is completed in a two step process consisting of:

1. The selection of the cleanup approach; and

2. The selection of the specific cleanup technologies.

The primary goal of cleanup efforts is to reduce the risks associated with specific pathways at a site to an acceptable level of risk in the most cost-effective manner. The cleanup approach should be developed for each pathway of exposure resulting in an unacceptable risk. The site investigation completed at the site should provide the information and data needed to select the cleanup approach and cleanup technologies.

Selection of the Cleanup Approach

In developing a comprehensive plan of the cleanup approach for a site where pesticides have been released to the soil and groundwater, the following factors should be considered:

- Nature and distribution of the pesticides and breakdown products;

- Exposure pathways;

- Environmental risks (liabilities);

- Cost-effectiveness and feasibility of cleanup technologies;

- Regulatory agency requirements;

- Current and future land uses;

- Concerns of the community; and
- Schedule for cleanup.

It is apparent that the selection of a cleanup approach will be very site-specific and will not be limited to technological considerations.

As a brief example of a site-specific cleanup approach, we could consider a hypothetical site where shallow soils have been contaminated with a relatively immobile pesticide. After consideration of potential exposure pathways and possible risks, it may be determined that soil removal or treatment are not necessary to meet the cleanup objectives. This conclusion would dictate a cleanup approach consisting of source area control. With this approach, the viable cleanup technology will be selected from a broad range of alternatives available for capping or otherwise isolating the contaminated soil from possible receptors, and from contact with percolating surface water, if applicable. This approach will narrow the range of technical options to be evaluated in detail and permit the designers to direct any additional site characterization work, if necessary, toward resolving any specific data deficiencies associated with the viable cleanup approach.

SELECTION OF SPECIFIC CLEANUP TECHNOLOGIES

Following identification of an overall cleanup approach the viable cleanup technologies or combination of technologies must be evaluated. The individual technologies must be configured to meet site-specific constraints identified in the selection of an overall approach.

Two broad categories of technologies are discussed in this paper:

- Conventional Technologies
- Developing Technologies

Conventional cleanup technologies are defined here as those technologies which have been demonstrated to be successful on a full-scale basis. Examples of conventional technologies include landfill disposal of solid waste, site capping, granular activated carbon adsorption, etc.

Developing technologies are defined here as those which have been demonstrated on a pilot scale or under highly controlled or specific conditions. In situ biological treatment of pesticides in soil or groundwater may be considered a developing technology, for example.

Conventional Cleanup Technologies

The typical potential pathways through which human exposure generally may occur as a result of an uncontrolled release of pesticides to soil and water are:

1. Direct contact with soil containing pesticides.

2. Contact with surface runoff from and drainage through the soil containing pesticides.

3. Using the surface or groundwater containing pesticides for a drinking water supply.

In Table 1, examples of cleanup approaches and conventional cleanup technologies for mitigating potential movement through these pathways are presented along with pertinent factors affecting the selection of a specific technology.

Developing Technology

In-situ soil treatment through the addition of amendments to stimulate microbial breakdown of pesticides is being investigated at several sites in California. The low cost of incorporating fertilizer or other amendments to create optimal environments for microbial activity compare favorably with offsite disposal costs. In addition, future liability may be reduced when compared with offsite disposal of hazardous wastes.

Aboveground evaporation beds are also being investigated. In this process water flows up through the soil and evaporates. Both aerobic and anaerobic conditions are developed, increasing the number of potential pathways for chemical degradation. While this research has been directed at the treatment of rinse water generated in limited volumes, it may be useful for treating low volumes of extracted groundwater, or as on-site treatment of surface soil "hot spots".

The EPA is currently funding efforts to identify enzymes capable of degrading pesticides into non-toxic products. Researchers have shown that methyl parathion hydrolase is effective in the degradation of parathion. The addition of a similar enzyme may some day prove to be a cost-effective amendment in certain situations when incorporated with a microbial stimulation program.

New groundwater treatment technologies, such as spray irrigation and land application, are also being investigated. Examples are shown in Table 2. As yet, cost-effective treatment systems using these technologies, mobile or stationary, are not available but the outlook is encouraging.

TABLE 1

EXAMPLES OF CONVENTIONAL CLEANUP TECHNOLOGIES

Cleanup Approach	Examples of Cleanup Technology	Applicability	Regulatory Requirements	Risks
Source Area Removal	Soil excavation & offsite disposal	o Limited soil volumes o Shallow soils	o Landfill permitted for waste o Emissions generated during excavation must be controlled	o Continued liability for wastes
Source Area Control	Soil capping	o Low levels of pesticides in soils o Pesticides with low mobility	o Continued monitoring of soil or groundwater o Engineering/site investigation may be more extensive than for removal	o Impact on future land uses o Site is not "clean" o Future releases could still occur
Groundwater Treatment	Air stripping	o Volatile organics o Mobile organics	o Limit on air emissions o Risk assessment on air emissions o Disposal of treated effluent	o Efficacy and duration of extraction program may not be accurately predicted
	Carbon adsorption	o Wide range of pesticides	o Disposal of treated effluent	o Regeneration/disposal of carbon beds o Costs can be highly variable if waste is not adequately characterized

IDENTIFICATION AND REMOVAL OF HYDROCARBONS FROM UNCONSOLIDATED SEDIMENTS AFFECTED BY TIDAL FLUCTUATIONS

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ABSTRACT

Multiple product losses occurred in a petroleum tank farm through its 80-year history. Accumulation of the product on the water table and subsequent migration resulted in seepage from the site into an adjacent creek. A thorough hydrogeological investigation was designed to identify variation in the subsurface which controlled migration of the hydrocarbons. Geologic logging of the soils, geophysical surveys, and aquifer tests revealed the presence of abandoned stream channels which acted as preferred conduits for the movement of the hydrocarbons. Interlayed fineand coarse-grained sediments resulted in the formation of natural traps where oil preferentially accumulated. Three major "pools" were located and an eight-inch recovery well was installed in each pool. Water table depression pumps placed in these wells created cones of depression which induced oil from the aquifer. Complications in the recovery method due to tidal fluctuations and changes in pumping level caused by mineral precipitation in the well and depression pumps were overcome by the use of an Auto-Skimmer to recover the floating hydrocarbons. This equipment automatically compensated for the changes in water level and product thickness, and was used to successfully recover over 24,000 gallons of product in the first 240 days of the operation.

Additional application of the Auto-Skimmer in a monitor well adjacent to the creek without a water table depression pump resulted in additional product recovery. The recovery effort presently continues with noticeable decrease in oil seepage to the creek, oil thickness in the aquifer, and oil recovery rate.

INTRODUCTION

On November 23, 1981, an oil slick was observed on a tributary to the Delaware River adjacent to a petroleum storage terminal in northeastern New Castle County, Delaware. The oil was being discharged to the stream from the stream bank, and upon detection, a containment boom was immediately erected by terminal personnel to prevent discharge of the oil to the Delaware River.

An initial subsurface investigation was conducted by terminal personnel utilizing a backhoe. They made excavations to the shallow water table and determined the presence of free petroleum products. A

26-inch diameter well equipped with a floating oil skimmer was installed in the vicinity of the stream to begin immediate petroleum recovery. Although the recovery well adjacent to the stream recovered over 5,000 gallons in its first two months of operation, the oil seepage into the creek continued unabated.

Location and Setting

The oil storage terminal is located on the flood plain of the Delaware River in northeastern New Castle County, Delaware (see location map, Figure 1). The site is fronted by the Delaware River on the south and bounded by a tributary to the river on the southwest.

Site History and Facilities

Generally, the oil storage terminal has been in use since the early 1900's. It was originally constructed as an asphalt refinery, and product storage at the time was predominated by wooden casks which were pile two to four tiers high and occupied a good portion of the site. Presently, little is left of the former asphalt refinery, and the locations and status of abandoned buried pipelines are unknown.

During World War II, the terminal experienced much activity unloading high octane gasoline from railroad tank cars and transferring it to river barges for shuttle to overseas wartime convoys. The former off-loading area for the tank cars is presently on the west side of the site, and buried pipeline location and abandonment status are also unknown.

Products historically stored on the site have included asphalt oils, heavy and residual oils, fuel oils, gasoline, and petroleum distillates. These products were transferred through two major pipeline arteries which run north-south through the site (Figure 2). During the life of the terminal, many of these pipelines were initially underground. Failures of the lines occurred as a combination of the age of the facility, the lack of cathodic corrosion protection, and the inability to inspect and maintain the subsurface pipelines. Many pipeline leaks historically occurred in the northeast quadrant of the site. The majority of these leaks resulted in small unrecovered and unaccountable losses indistinguishable from natural fluctuations in inventory due to temperature. In 1979, one failure on the east side of the site resulted in a loss of more than 13,000 gallons of gasoline.

SUBSURFACE INVESTIGATION

Soil borings were drilled using mud rotary and split-spoon techniques in 21 locations on the 25-acre site (see Figure 2). Many of these borings were performed in areas of known product residence as defined by the initial back-hoe investigation. Other borings were performed in other parts of the site in order to correlate sedimentary materials and define the hydrogeologic system. Soil samples were collected continuously from grade level to bedrock, which occurred at a depth of approximately 18 to 25 feet below grade. Two-inch monitoring wells were installed in each boring with sufficient well screen to expose the entire aquifer and allow monitoring of the free water surface.

The geologic materials encountered by the borings represented a sequence of stream derived (fluvial) deposits termed the "Trenton Gravels" (Owens and Minard, 1979) overlying a weathered bedrock surface. This sequence graded upward from coarse sand and gravel to a fine sand (generally 10 feet to 15 feet thick), overlain by a clayey silt (7 feet to 10 feet thick).

In an effort to gain a more complete understanding of the subsurface structure in areas where borings were not possible, geophysical exploration using a Soiltest R40C Earth Resistivity Meter with the Wenner electrode array was employed (see Roman, 1960; 1966; and Soiltest, 1968, for information on earth resistivity).

The soil borings and geophysical survey indicated that the subsurface of the site was laced with abandoned stream channels. A major abandoned channel traversed the site from east to west, dipping below the water table along its entire length. This channel was composed of silt and consequently was low in permeability. It trended across the predominant groundwater flow direction (see Figure 3), as established by measuring head potential elevations in the monitoring wells, and intercepted floating petroleum products which migrated from spill sites upgradient.

Observation of the character and thicknesses of oil in the monitoring wells indicated the presence of three product accumulation "pools" distributed across the center of the site (see Figure 4). These "pools" were apparently stratigraphically trapped by the abandoned channel as modeled in Figure 5. Sampling of the free product indicated that each pool differed from the other in compositions, displaying various mixtures of gasoline, fuel oil, and kerosene. The pools appeared to be vertically stratified by gravity, with the gasolines occurring at the upper fluid surface and the heavier oils occurring at the oil water interface. This stratification indicated the variety of product spills on-site, as well as the time the products resided in the subsurface.

One of the pools was adjacent to the stream, which cross-cut the aquifer and received much of the groundwater discharged from the site. The hydrocarbon discharge from this pool into the stream occurred at a relatively slow rate because of the low water table gradient, the reversal of groundwater flow in the vicinity of the creek due to its tidal fluctuation, and a low permeability of the stream channel lining.

During the history of the site, most of the oil was held immobile by the abandoned silted-in channel present in the flood plain sediments. However, during times of peak groundwater stage, migration between pools occurred. This migration during the winter months of 1981 resulted in the discharge to the stream.

HYDROCARBON RECOVERY MEASURES

Although the water table was only 8 to 10 feet below grade and easily accessed with a trench, utilization of recovery wells was chosen to facilitate active manipulation of the groundwater flow system and to avoid difficulty with buried pipelines and other facilities. Tidal action and seasonal groundwater stage fluctuations also necessitated the use of a recovery well rather than a trench.

Hydraulic testing of the monitoring wells employing the slug test (see Bouwer and Rice, 1976) was used to determine the number of recovery wells required for recovery. These tests indicated that one recovery well installed in each of the three major oil accumulation pools would provide the necessary groundwater control.

The wells were drilled following initial pilot boring and sampling to establish the vertical sequence for optimum well screen design. The wells were eight inches in diameter and were installed using mud-rotary open-hole (12-inch) techniques. The well screen was gravel packed, continuously wound steel, with slot sizes varying according to the sedimentary texture. The wells were developed using air surging and water jetting to sufficiently remove fine materials from the well bore and create sand-free pumping conditions.

Following development, each well was hydraulically tested to determine its maximum sustained groundwater yield. Water table depression pumps were selected according to available power, groundwater withdrawal requirements, pipe diameter, and distance to the discharge points. Intrinsically safe water level controls were installed to prevent oil intake by the pump.

Pumped groundwater was discharged to the plant stormwater system, which ran through the plant oil/water separator prior to discharge to the Delaware River (Figure 2). An amendment to the existing NPDES

permit covering the oil/water separator was required prior to initiation of pumping activities.

An Auto-Skimmer was deployed to recover the floating hydrocarbons from each recovery well. This oil recovery equipment was developed by R. E. Wright Associates, Inc. in response to requirements for a versatile and effective recovery; it was utilized in this application because of anticipated variations in product viscosity and pumping water levels. The Auto-Skimmer works by periodically lowering a closed end bailing vessel into the fluid of the well bore, skimming the surface, and returning it to grade level for emptying. The vessel is pumped into an integral separator which routes the oil to a tank and returns the water to the well. The Auto-Skimmer effectively kept the water surface of the recovery wells free of hydrocarbons, removing the various products which resided under the site. The units automatically compensated for changes in pumping water level in the recovery wells due to variations in groundwater pumping rate, tidal fluctuations, and depression pump failure.

Following a three-week start-up time, site visits were performed on a weekly basis. These visits were utilized to monitor groundwater levels and oil thicknesses in monitor wells, gage and empty recovery tanks, and maintain recovery equipment. The recovery system operated automatically during the intervening week.

HYDROCARBON RECOVERY RESULTS

Groundwater Control Area

Groundwater was pumped from each recovery well, creating a cone of depression in the groundwater table. The resultant gradient imposed on the groundwater flow system by the cone of depression created a groundwater control area within which all flow was directed toward the recovery well. This induced oil to flow into the well for recovery.

Although a maximum control area was desired, initial pumping rates were conservative at about two-thirds maximum calculated yield in order to avoid entrainment of oil in newly exposed sediments. RW-1 was hydraulically tested and appeared capable of producing greater than 20 gallons per minute (gpm) on a sustained basis, but the start-up rate was 15 gpm. RW-2 was determined to be capable of producing 30 gpm and was limited initially to 15 gpm. RW-3 had a potential for 15 gpm but was started at 10 gpm. Figure 6 shows the development of the groundwater control area at these flow rates as measured in the monitor wells at a pumping duration of about one month. The measurements indicated that the pumping influenced the entire area occupied by the oil.

Each recovery well was started independently in turn. It was observed for drawdown and product influx for one week prior to producing interference by starting an additional recovery well. Observations of drawdown and oil thickness in surrounding monitor wells were used to determine aquifer parameters and groundwater control area. Fluid surface and water interface depth were measured with an Oil-Water Sonic Interface Probe by Marine Moisture Control Company, Inc. This instrument distinguishes between product and water using a combination of ultrasound and conductivity. Measurements were corrected for product gravity prior to analyzing groundwater head potential.

Oil thickness decreased in the monitor wells located greater than 50 to 100 feet from the recovery well, indicating migration toward the pumping center. Monitor wells located near the recovery well displayed an increase in oil thickness due to oil influx.

During the initial recovery effort, oil remained adjacent to the creek allowing for oil seepage to continue. In response, an additional Auto-Skimmer was installed on a monitor well adjacent to the creek. Operating without a depression pump, this unit removed over 100 gallons within the first month of its installation. This equipment in combination with the pumping influence of the recovery wells abated the seepage to the creek.

Oil Recovery Rate

Generally, oil recovery commenced with an initial "slug" of oil, induced from the immediate more permeable area surrounding the well bore. Following removal of this early yield, oil recovery rate remained low for several days while the control area established itself. Maximum oil recovery rates were established within three to five weeks following initiation of groundwater withdrawal (see Figure 7). RW-1's recovery rate was comparatively low, averaging about three-fourth gallon per hour. This rate remained consistent throughout the initial six months of the recovery effort despite reduction of groundwater yield, which occurred during this time. The maximum oil influx rate produced by RW-2 was about five gallons per hour, and RW-3's maximum was greater than eight gallons per hour. RW-2 and RW-3 recovered oil at a greater rate than RW-1 because of the loss of groundwater yield by RW-1, the greater oil volumes available to RW-2 and RW-3, and the more favorable locations of these wells with respect to their pools and local permeabilities.

Oil influx rates declined substantially in RW-2 and RW-3 following maximum influx peaks. These declines occurred because of the rapid removal of oil from the immediate vicinity of the wells and the decrease in pumping influence on oil residing at incremental distances from the recovery wells.

The Auto-Skimmers maintained product-free fluid surfaces in the recovery wells during their periods of maximum oil influx. The variable timer controlling the frequency of the skimming cycle was adjusted to operate at a slightly greater rate than the anticipated oil influx rate. As the production rates decreased, the frequency of skimming was proportionately reduced.

Oil Recovery Success

Cumulative oil recovery has attained over 27,000 gallons as of the date of this writing. The majority of that oil was recovered within the first six months of the project. As oil recovery rates declined, a simultaneous reduction in monitoring well oil thickness was observed. Additional oil remains in the subsurface of the site and the Auto-Skimmer continues to remove oil.

The estimation of initial and remaining subsurface oil was made difficult by the problem of estimating oil thickness in an aquifer using observations gathered with monitoring wells, as described by T. L. dePastrovich (1979). This investigator contends that the oil accumulated in monitoring wells is greater in thickness than that existing in the aquifer.

CONCLUSION

Multiple unaccounted for product losses occurred in the petroleum storage facility through its 80-year history. The unrecovered hydrocarbons accumulated on the groundwater table in three distinct pools across the center of the site. Migration of one of the pools resulted in seepage of the oil from the site into an adjacent stream.

An oil recovery plan was devised following a detailed hydrogeologic investigation. This plan called for the installation of three eight-inch wells: one in each major accumulation pool. Groundwater depression pumps were installed in each well to create a cone of influence and to induce oil to flow into the well. Three Auto-Skimmers were employed to removed oil from the three recovery wells. The Auto-Skimmers effectively recovered accumulating product from their recovery wells in quantities as great as nine gallons per hour. The Auto-skimmer automatically compensated for changes in water level in the recovery wells due to tidal fluctuations or changes in pumping level. The recovery effort was completely automatic and required only weekly visits to monitor wells, gage and empty recovery oil tanks, maintain groundwater depression pumps, and adjust pumping rates.

The effort removed over 24,000 gallons of free product within the first 8 months. Simultaneously, reduction in monitor well oil thicknesses and seepage to the stream have occurred.

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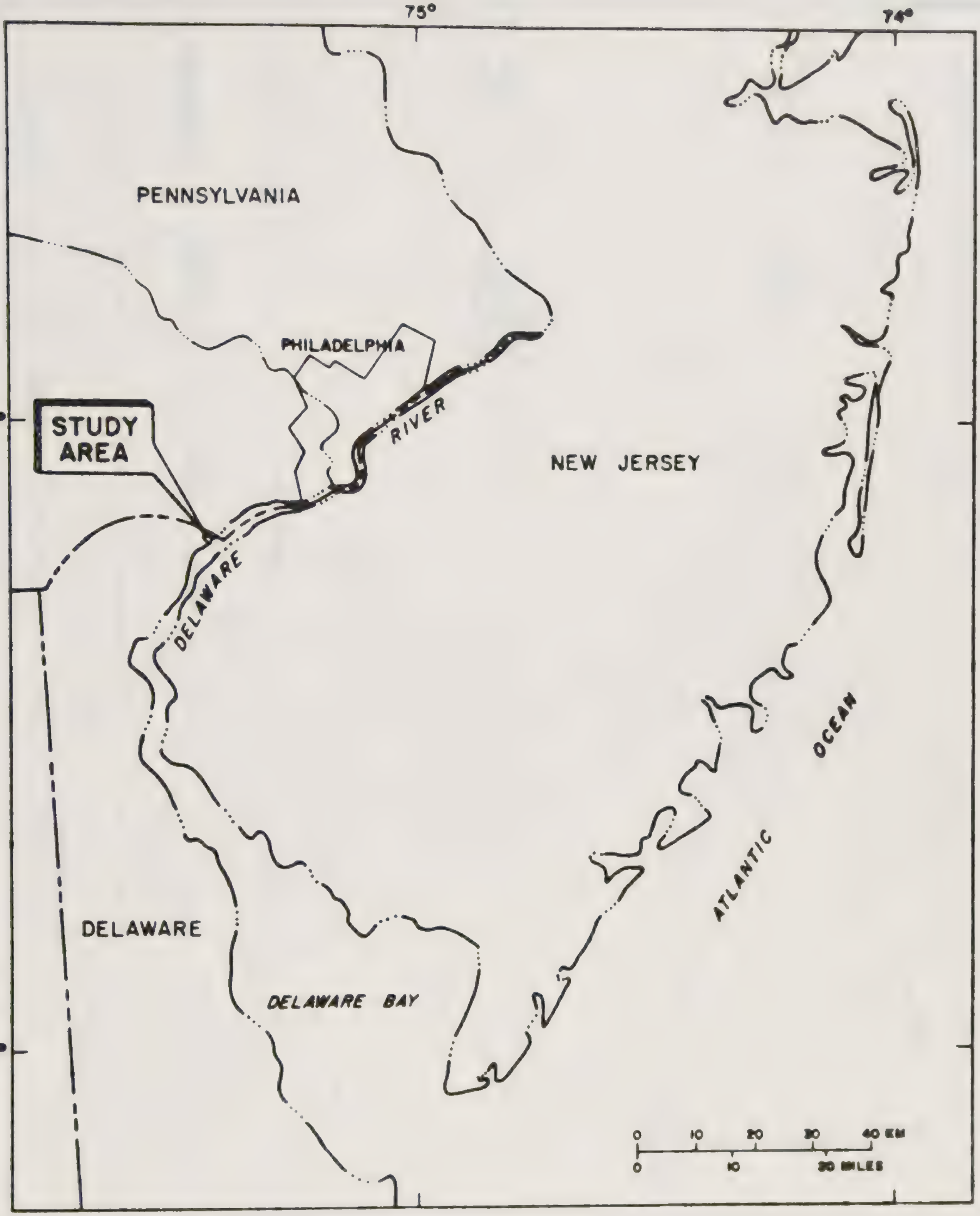

Figure 1 : Site Location Map Indicating Possition of the Study Area on the Delaware River (modified from Owens and Minard, 1979).

Figure 2: Site Facilities Map Indicating Locations of Product Pipelines, Documented Historic Spill Sites, Monitoring and Recovery Wells, and Pumped Groundwater Treatment.

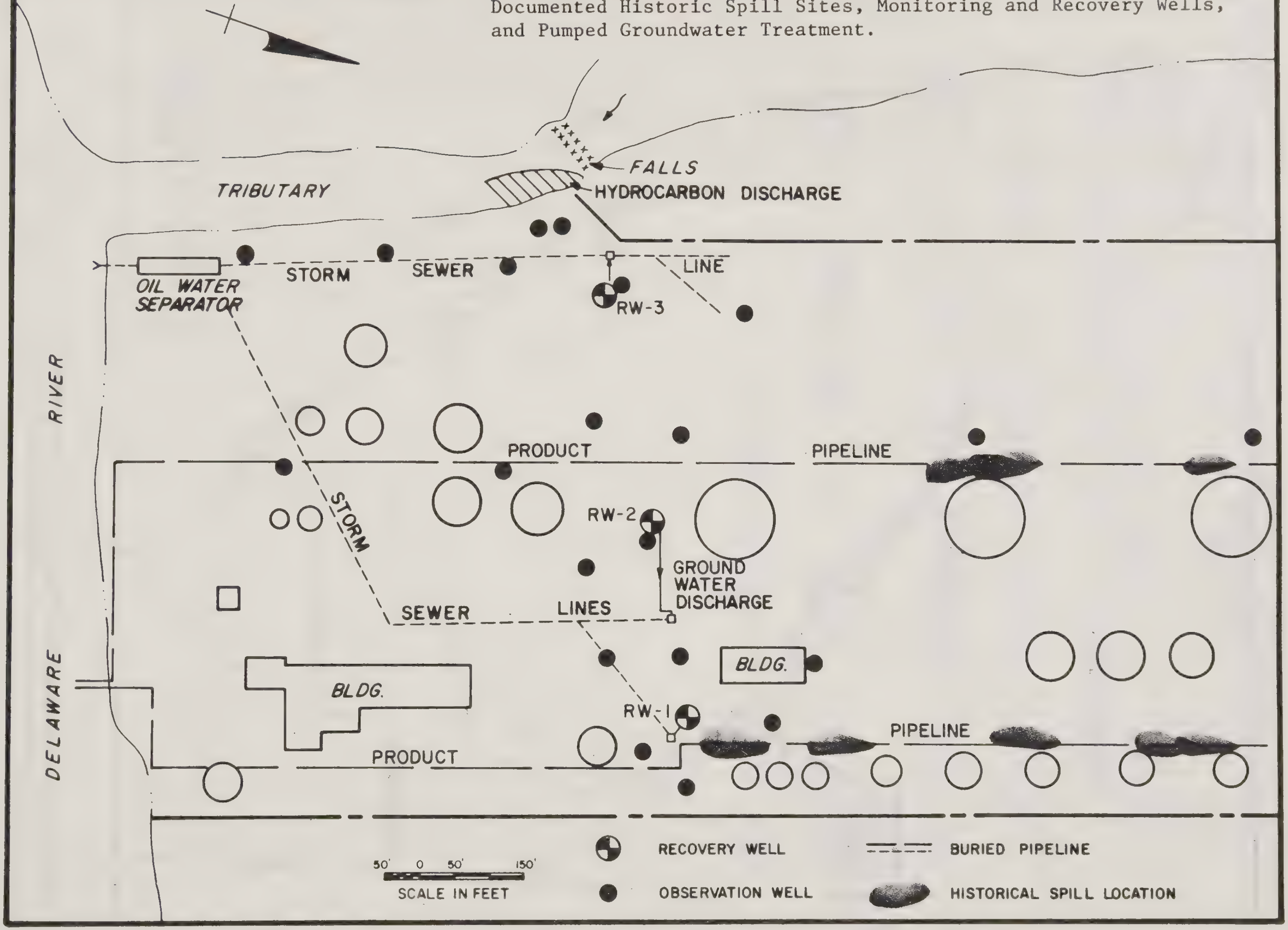

FIGURE 2

Figure 3: Map of the Silted in Channel Where it Dips Below the Mean Groundwater Table Showing its Orientation Across the Groundwater Flow Direction.

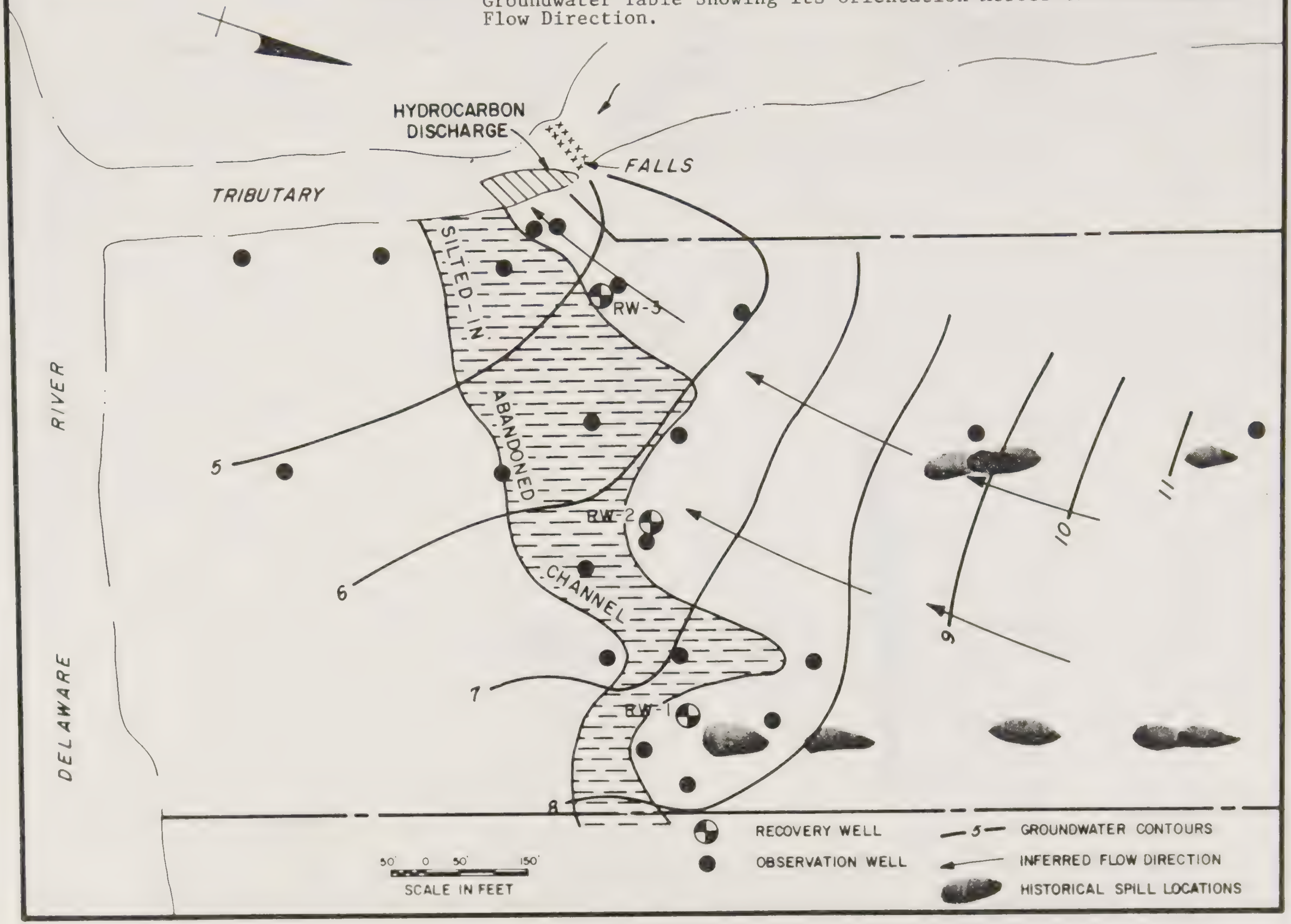

FIGURE 3

Figure 4: Map Showing Location of 3 Subsurface Oil Accumulation "Pools," and Their Thicknesses as Measured in Monitoring Wells Before Oil Recovery.

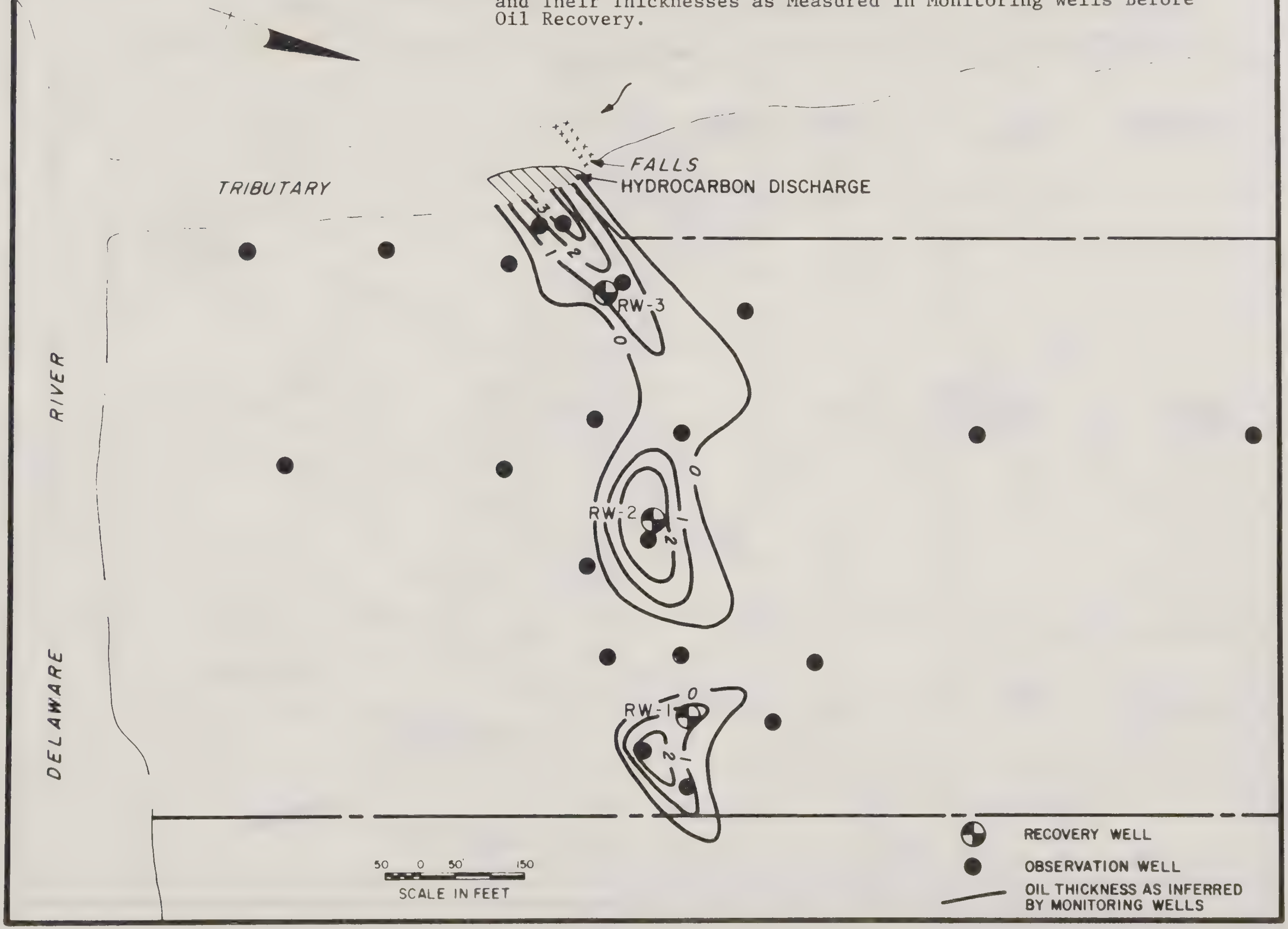

FIGURE 4

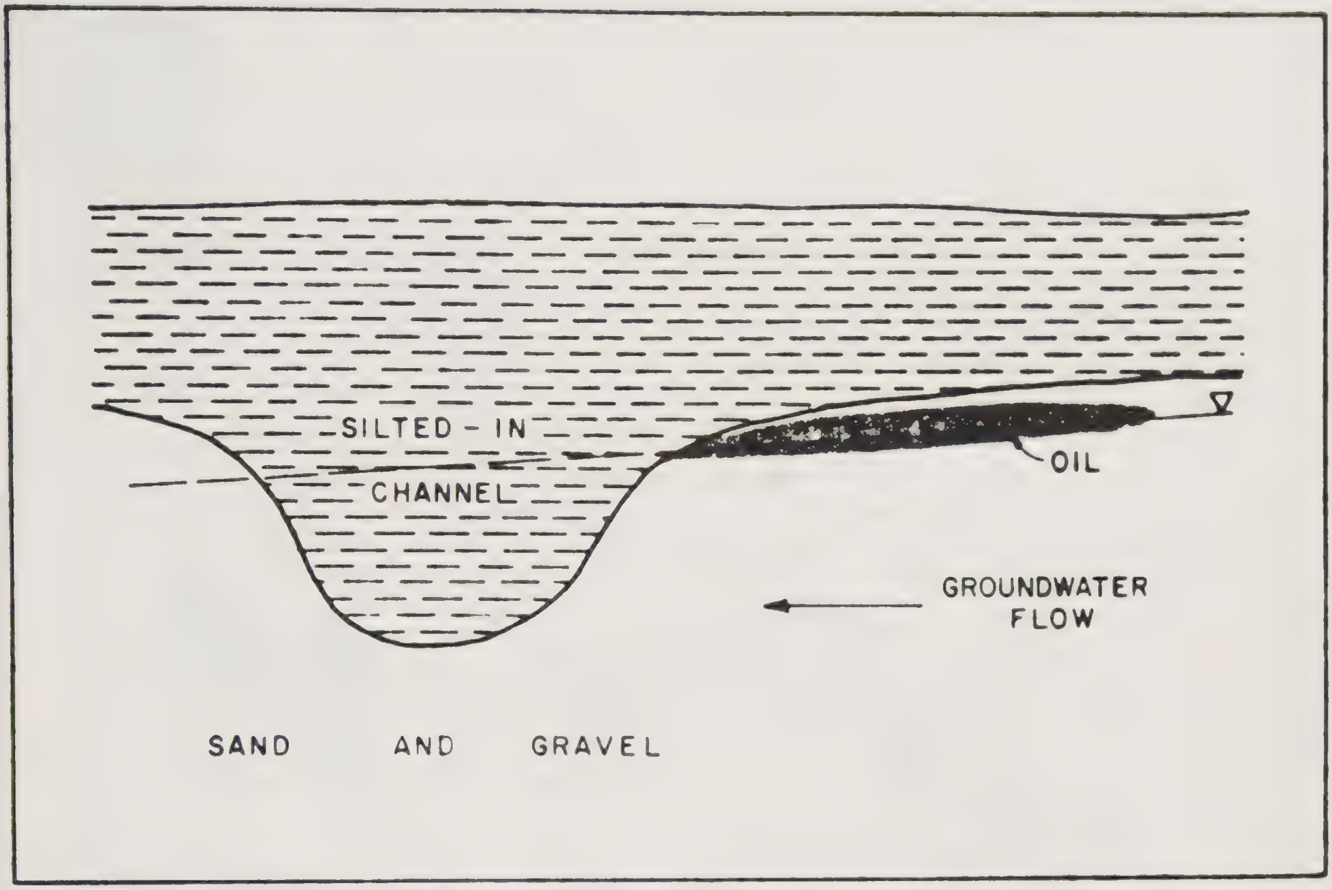

Figure 5 : Schematic of Stratigraphic Oil Trapping by Abandoned Channel Deposit at the Groundwater Surface.

Figure 6: Map of Groundwater Control Area Induced by Pumping Recovery Wells. Shaded Area Indicates Location of Oil Prior to Initiation of Pumping and Recovery

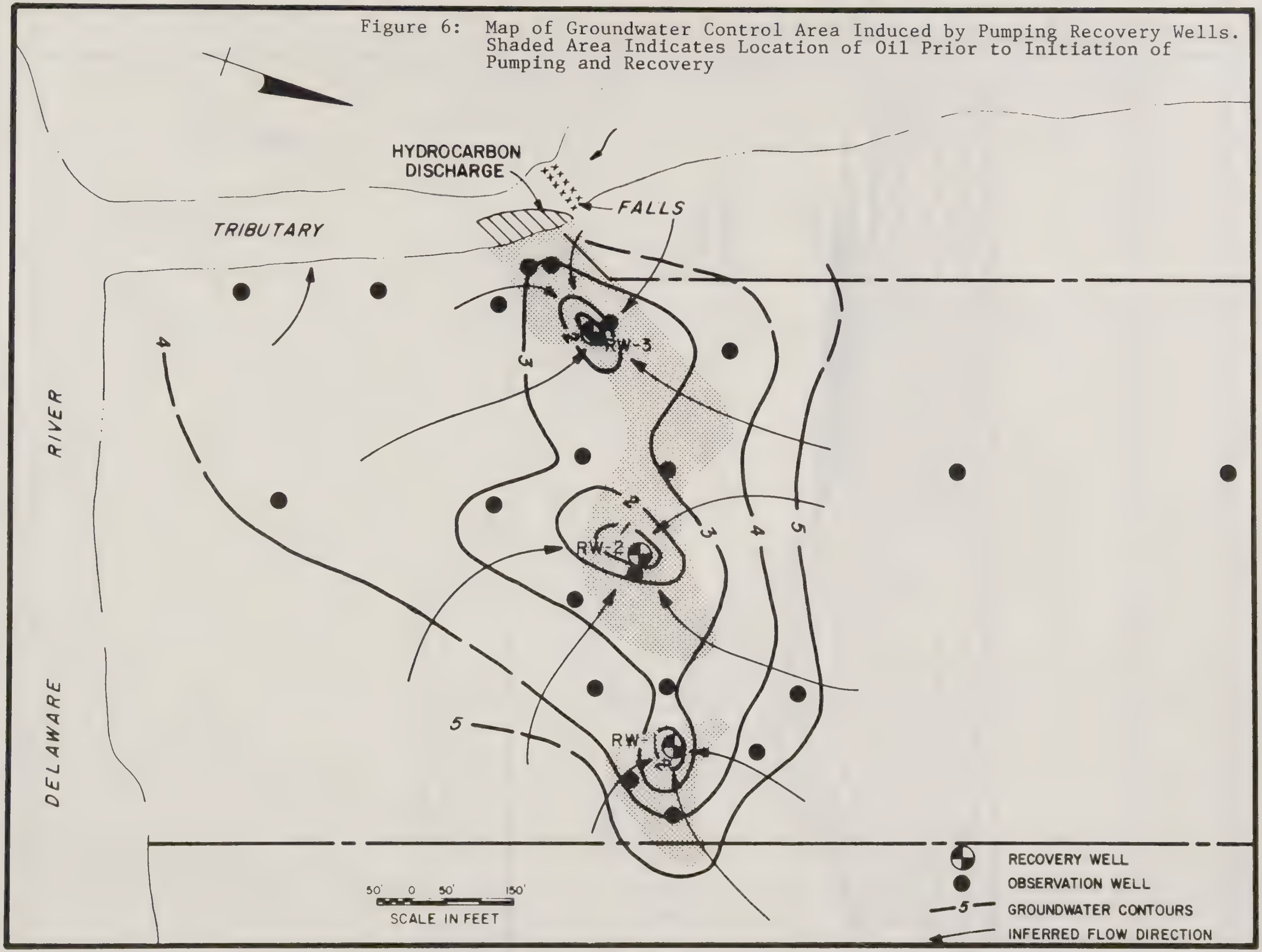

FIGURE 6

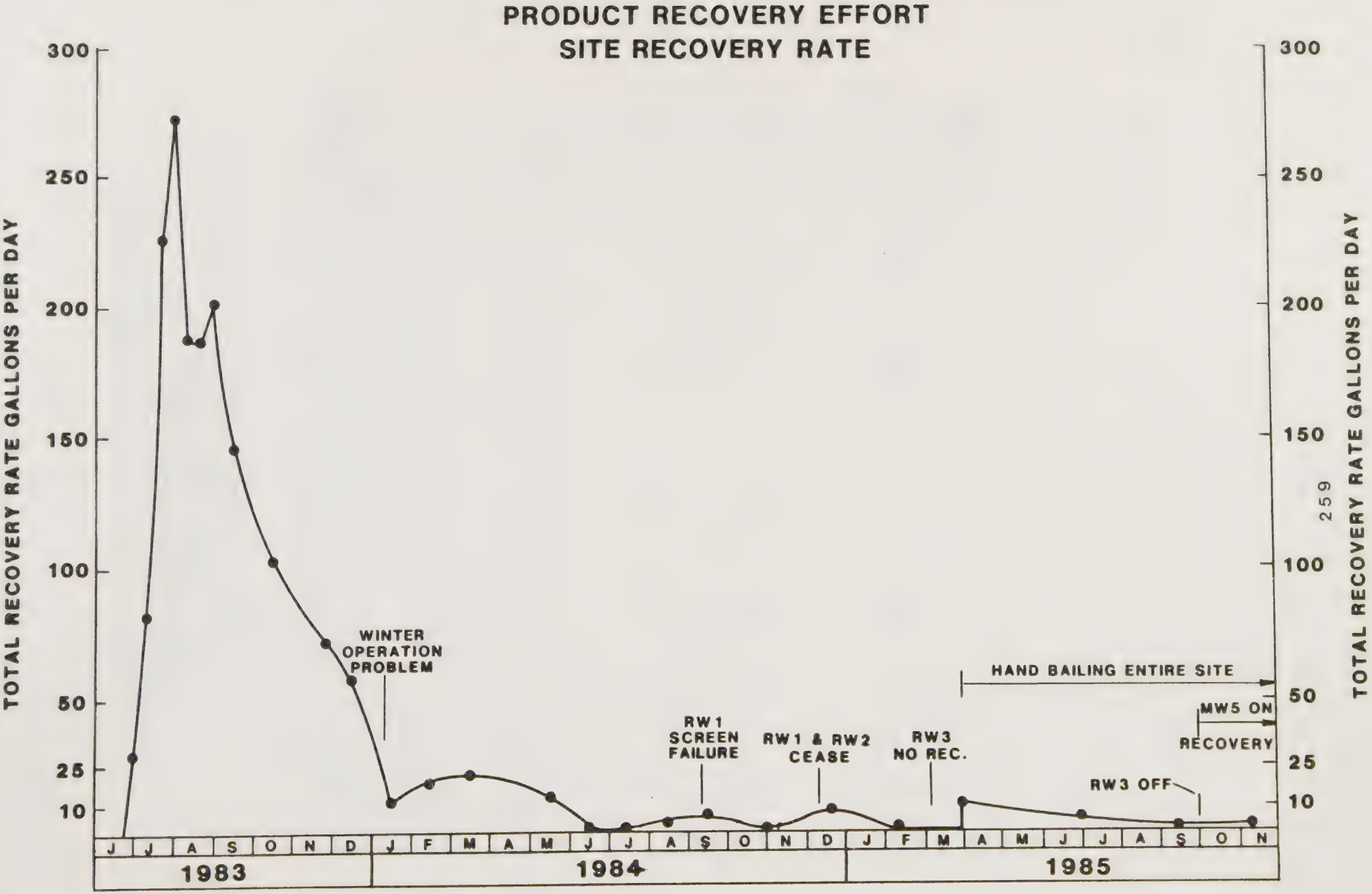

Figure 7: Historical Site Recovery Rate Curve for Product Recovery Effort.

RCRA CLOSURE FOR A METAL RECYCLING FACILITY

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Recently, economic analysts have observed that the United States is in the midst of a major shift from a manufacturing or product based economy to a service based economy. This shift is substantiated by reports of manufacturing plant shutdowns across the nation. These plant shutdowns may seem straightforward but, in many instances, there is more to facility closure than simply closing the doors, locking the gates and walking away.

Industrial plants which generate hazardous wastes in their manufacturing process are required to be operated and closed in accordance with requirements of the Resource Conservation and Recovery Act (RCRA). The methods for fulfilling the RCRA requirements vary considerably based on site characteristics, facility operations and the owner's future plans for the site. Consequently, a flexible approach should be taken to site closure with closure activities tailored to the facility operations and site characteristics. To illustrate the importance of a flexible approach, the discussion that follows will focus on a case study highlighting how a RCRA closure plan for a metal recycling facility in the western United States was developed, negotiated, and executed.

RCRA CLOSURE

As a condition of acquiring an operating permit as a hazardous waste treatment storage or disposal facility (TSD), the facility must prepare and submit for agency approval[1] a Closure Plan describing how the facility will be closed. The facility must be closed in a manner that:

1) "Minimizes the need for further maintenance, and

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[1]Depending on location, this may be the EPA or a state agency.

2) controls, minimizes or eliminates to the extent necessary, to prevent threats to human health and the environment, post closure escape of hazardous waste, hazardous waste constituents, leachate, contaminated rainfall or waste decomposition products to the ground or surface waters or to the atmosphere."[2]

Uniform cleanup standards for site closure are not specified by RCRA. The actual mechanics of how a facility will be closed and the concentrations of chemicals that will be permitted to remain on a site after closure are determined on a case-by-case basis through negotiations between the facility owner and the regulatory agency. There are no requirements under RCRA for the absolute removal of all hazardous wastes from a facility for closure. Chemical concentrations in excess of hazardous waste standards may be permitted to remain on the site provided the regulatory agency is convinced that residual chemicals do not pose threats to human health and the environment.

CASE STUDY

The importance of a flexible approach to site closure is illustrated by the closure of a metal recycling facility in the western United States. The facility operated a detinning plant for approximately 60 years beginning in the 1920's. Scrap metal, predominantly in the form of cans, was shipped in as a raw material, shredded and then chemically treated to remove tin. The stripped tin, which was contained in an aqueous solution, was recovered through an electroplating process which resulted in the deposition of metallic tin on electrodes. The electrodes were then heated to melt the metallic tin deposits. The tin was then solidified into ingots for sale. Wastes containing lead, zinc, tin, and other metals were generated in both aqueous and sludge forms. In 1982, the plant ceased detinning operations and notified the responsible regulatory agencies of its intent to close the interim status hazardous waste management facility.

A closure plan was initially submitted and subsequent addenda were incorporated into the approved Closure Plan as

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[2]Closure Performance Standard as specified in 40 CFR 264.111.

site cleanup progressed. The Closure Plan was based upon two objectives: 1) to remove all commercial waste products from the site and 2) to ensure that no threat to human health and the environment will remain after closure.

To facilitate a systematic removal of all commercial waste products the 20 acre site was divided into four zones. Waste products in the form of liquids, sludges, and associated soils were removed from each of the zones and disposed of at an approved hazardous waste disposal facility. Two underground gasoline and oil storage tanks were emptied, chemically flushed, and transported to an approved disposal facility.

Following waste product removal, verification sampling of remaining soils was performed. Samples were collected from several locations in each of the four zones with and analyzed for lead and zinc. Site-specific cleanup standards for soil were negotiated based on federal Extraction Procedure (EP) Toxicity criteria for soluble lead.

Several sampling locations were identified as containing lead in soil at concentrations greater than the EP Toxicity standard. For each zone containing elevated concentrations of lead, a subclosure plan was submitted to and approved by the regulatory agency. Subclosure plans called for removal of additional material until lead concentrations were below 500 mg/kg. This 500 mg/kg level for total lead was determined during negotiations with the regulatory agency. Following soil removal and resampling, clean fill would be imported to these areas.

Additional industrial sludges were removed from the basements of two buildings on the site. Sludge was transported to an approved hazardous waste disposal facility for disposal and basements were broom swept clean. Post cleanup verification was provided by wipe samples collected from the basement floors. Samples were collected by wiping a 100 cm^2 area of the floor with moistened filter paper. The regulatory agency concurred that broom sweeping provided an acceptable level of lead removal based on concentrations of 38 mg/100 cm^2 and less in the wipe samples.

Consistent with the second closure objective of ensuring that no threat to human health and the environment will remain, assessments of surface water runoff and groundwater in the vicinity of the site were conducted. The scope of these investigations was negotiated with and approved by

the regulatory agency. Groundwater sampling was divided in both deep and shallow zones. Four onsite monitoring wells were installed in the deep zone. Samples were collected and analyzed for pH, lead, zinc, tin, cyanide, total organic carbon, and total organic halogen. Concentrations were at sufficiently low levels for regulatory agency agreement that no further investigation was required.

Eighteen groundwater monitoring wells were installed in the shallow zone with 12 onsite and six in offsite areas. Samples collected from these wells were analyzed for lead, zinc, iron, cyanide and pH. Results for total lead analyses indicated the presence of lead in shallow groundwater. However, further examination revealed that lead concentrations were associated with subsurface sediments and soluble lead concentrations were low and hence not of concern. Based on analytical results, the shallow groundwater investigation was accepted by the regulatory agency.

Surface water runoff samples were collected from an onsite storm water detention area after four rainfall events. Standards for maximum concentrations of lead, cyanide, oil and grease, and tin in runoff water from any single rainfall event were established after negotiations with the regulatory agency. No daily grab samples or event composites exceeded these standards. Agency requirements for surface water runoff control were met by the future remedial action of placing clean fill over soil in the western portion of the site.

Once the agency-approved Closure Plan has been developed, and implemented, steps remaining are certification of closure, final agency approval, and post-closure care, if necessary. RCRA requires certification by both the owner or operator and an independent registered professional engineer that the facility has been closed in accordance with the approved closure plan. For facilities where hazardous waste will remain after site closure, a post closure care and monitoring program must be developed. This program is based on waste and site characteristics, and can have a duration of 30 years or more. For the case of this metal recyling facility, the owners did not want to be committed to any post closure monitoring and thus chose to remove all hazardous wastes from the site.

As this case study of a metal recycling facility has shown, RCRA closure for a hazardous waste management facility is a very site-specific process. Removal of all

hazardous wastes from the site is not necessarily a requirement for closure. Initially, a closure plan must be negotiated with the regulatory agencies and cleanup standards established. The plan and standards should be based upon the site characteristics, facility operations, and the owner's future plans for the site. In any event, a flexible approach tailored to the particular facility is the key to a successful and cost-effective RCRA closure.

LANDFILL CONTAINMENT METHODS

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The California Administrative Code, Title 23, Chapter 3 - State Water Resources Control Board, Subchapter 15, Waste Disposal to Land, was adopted October 18, 1984; thus, the consulting industry has about 1-1/2 years of experience with implementation of these regulations. Extensive portions are devoted to containment of wastes.

By now, all concerned parties are aware that Class I wastes are hazardous, Class II wastes are hazardous under certain conditions, and Class III wastes are not hazardous. The drafters of these regulations went into extreme detail in describing the differences among the required conditions for disposal. Among other requirements, "Class I disposal units shall be located where natural geologic features provide optimum conditions for isolation of wastes from waters of the state." And, "...Class I units shall be immediately underlain by natural geologic materials which have a permeability of not more than 1×10^{-7} cm/sec..." "Class II waste management units shall be located where site characteristics and containment structures isolate waste from waters of the state." And, "...Class II landfills or waste piles shall be immediately underlain by natural geologic materials which have a permeability of not more than 1×10^{-6} cm/sec..." "Class III landfills shall be located where site characteristics provide adequate separation between nonhazardous solid waste and waters of the state." And, "...Class III...landfills shall be sited where soil characteristics, distance from waste to ground water, and other factors will ensure no impairment of beneficial uses of surface water or of ground water..." The regulations continue, "Where...site characteristics alone do not ensure protection of the quality of ground water or surface water, Class III landfills shall be required to have a single clay liner with permeability of 1×10^{-6} cm/sec or less."

It should be obvious from the above that there is a decreasing emphasis on containment from Class I through Class III.

Under Article 4, Construction Standards, the regulations require that "Class I and Class II waste management units shall be designed and constructed to prevent migration of wastes from the waste management units to adjacent geologic materials, ground water, or surface

water, during disposal operations, closure, and the post-closure maintenance period." The regulations continue, "Class III landfills shall have containment structures which are capable of preventing degradation of waters of the state as a result of waste discharges to the landfills if site characteristics are inadequate."

This emphasis on containment introduces the key issue of permeability: "Permeabilities specified for containment structures...shall be relative to the fluids...to be contained. Permeabilities specified for final cover shall be relative to water." Furthermore, "permeabilities shall be determined primarily by appropriate field test methods..."

The requirement of field permeability testing has come as a surprise to most consultants and other knowledgeable observers. While most professionals in the field agree that field tests yield more reliable results than do laboratory tests, the field tests available today do not adequately test permeability. In fact, they measure infiltration rather than permeability.

That "permeabilities...shall be relative to the fluids...to be contained" raises the question of compatibility of liners and the fluids to be contained. The state provides a suggested methodology for compatibility testing that most practitioners have questioned. New methods are needed and are under development. For example, a paper presented to this conference by Suren Dakessian, Ph.D., presents a new approach to the development of compatibility testing.

The U.S. Bureau of Reclamation Designation E-19 has been a field test permeability standard for many years. It is most applicable to soils having permeabilities between 10^{-4} and 10^{-5} cm/sec. The apparatus cannot handle flows much above 10^{-4} cm/sec, and permeabilities of 10^{-6} cm/sec or lower require too long a testing period for test validity to be assured.

Double ring tests developed in recent years obviously are an improvement over E-19, because the use of the outer ring tends to contain the flow that infiltrates from the inner ring. Daniel and Trautwein* propose the use of a sealed double ring infiltrometer; this equipment overcomes evaporation and measurement problems. The main limitation of all infiltrometer tests is that they must be run for a long period--weeks, even months, for low-permeability materials. What is needed are other methods (perhaps approximation tests) which will place the permeability values within a bracketed range.

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* Daniel, D. E. and S. J. Trautwein, undated, "Field Permeability Test for Earthen Liners" (draft).

Subchapter 15 regulations also stress the need for monitoring. Under Article V, water quality monitoring, the regulations state: "Owners and operators of new and existing landfills...shall monitor ground and surface water...and shall perform unsaturated zone monitoring..." Again, this area of technology is characterized by inadequate instruments and procedures.

The only vadose zone (or unsaturated zone) monitoring methods that have obtained Regional Water Quality Control Board approval are suction lysimeter systems and nuclear probe access tubes.

Suction lysimeters have been used for years to take samples of ground water that is in transit in the subsurface. On the other hand, the installation of lysimeters beneath landfills is a relatively recent trend. A lysimeter essentially consists of a porous stone where water enters and is stored in a receptacle. Air pressure is applied through one tube, and water collected in the receptacle is forced out through another tube. Of course, if no water is collected, that is favorable, because no water means no leachate. Lysimeters work well if carefully installed, but long-term performance records may be suspect.

Because of the questionable long-term performance of lysimeters, we have proposed the redundant use of nuclear probe access tubes. These are simply small-diameter pipes sealed at the ground surface and brought up as the landfill surface is raised. The pipes are periodically opened and a nuclear probe is used to detect any changes in water content. An increase in water content suggests the presence of leachate. This system is sealed to enable detection of water content change, so a sample of the water cannot be obtained; it would be necessary to drill a separate boring to obtain a water sample. When installed in conjunction with lysimeters, nuclear probe access tubes should perform as a check on the presence of water (leachate) and should increase long-term monitoring capability.

In conclusion, an important challenge to professionals in the waste management business is to develop more effective means of determining the compatibility of liners and leachate, measuring permeability (infiltration) in the field, and monitoring the vadose zone for the presence of leachate.

DEVELOPMENT OF A LANDFILL REMEDIAL INVESTIGATIVE PROGRAM

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INTRODUCTION

Abandoned or improperly managed landfills may pose a significant threat to public health and the environment which must be addressed in a timely and effective manner. A case in point is a Class II-1 landfill in southern California where operational deficiencies and increasing public awareness prompted the development of an investigative workplan to address potential off-site hazards associated with the landfill. An initial remedial investigative approach was developed which addressed immediate public health and environmental concerns and long-term remedial solutions. While the approach discussed below was originally site-specific, it is intended to guide initial investigative efforts at other landfills representing varying degrees of hazard.

Scoping and Hazard Evaluation

Potential hazards associated with abandoned or improperly managed landfills may be conspicuous or unforeseen. Obvious conditions which appear to represent little more than a nuisance, such as odor episodes or leachate ponding, are often indicative of less apparent hazards. A method of fully determining the extent to which a landfill may threaten public health and the environment involves an evaluation of the following factors:

- The volume, chemical nature and physical state of wastes disposed,
- The effectiveness of any landfill management or control systems employed,
- The local and regional environmental setting, and
- The proximity to populated areas or sensitive receptors.

This type of preliminary hazard evaluation will assist in identifying hazards of immediate concern while addressing potential hazards requiring further investigation. The evaluation may be completed most cost-effectively by using existing information contained in landfill and regulatory agency files and in scientific journals. While a preliminary evaluation is necessary to prepare a scope of work for the initial investigative phase, an evaluation must be dynamic to incorporate new data generated in subsequent phases.

An evaluation of wastes disposed at the landfill will provide information regarding potential contaminants of concern, their toxicity, mobility and environmental fate. If control measures such as gas extraction, leachate collection or liner systems are in use, an evaluation of their design and operational history will provide an indication of the potential for migration of contaminants. Where control measures have not been installed or have proven to be inadequate, an evaluation of the local environmental setting including pedology, surface hydrology, hydrogeology and meteorology, will provide information regarding contaminant pathways. Finally, information on contaminants of concern, contaminant migration potentials and pathways must be applied in determining if a target and/or receptor population exists.

A target may be defined as a potable aquifer or surface water body such as a stream, lake or reservior or ambient air. A receptor population may include people who use a threatened aquifer on surface water body for drinking or agricultural purposes, individuals living or working in the vicinity of the landfill who may be exposed to toxic gaseous emissions or children who play on or adjacent to the site who may be exposed directly, via dermal or ingestion routes, to landfill contaminants.

Identification of a receptor population is critical in determining if initial or immediate remedial measures are necessary. Initial measures required will depend on the target and pathway and may include providing supplemental water supplies, installing a fence, applying additional cover material or installing or repairing a gas extraction and flare system. The intent of initial remedial measures is to abate immediate hazards during the development and implementation of subsequent phases of the remedial investigation. Identification of targets and a receptor population will also aid in refining and prioritizing subsequent phases of the investigation, focusing future work on those hazards most likely to impact public health and the environment. The effect of this refinement is a commitment of only those resources necessary to evaluate and develop relevant remedial solutions. If a systematic hazard evaluation is not completed early in the investigative phase, significant resources may be expended on characterization with the generation of data that have little or no bearing on the development of remedial alternatives.

DATA COLLECTION AND FIELD ACTIVITIES

The technical approach presented below was developed for implementation at Operating Industries, Inc. (OII) landfill in Monterey Park, California. Although it is specific to concerns identified at OII, the methodologies and field activities may be applied to other landfills as necessary.

Site Description

Operating Industries, Inc. landfill occupies approximately 190 acres and was in operation from the mid-1940's to December 1984. Designated a Class II-1 landfill by the Regional Water Quality Control Board (RWQCB), the landfill was permitted to accept liquid hazardous wastes in a specified 32-acre portion located in the western half of the site. Hazardous waste volumes are currently being determined based on an inventory of 80,000 manifests; recent estimates suggest that approximately 276 million gallons of liquid waste, including recycled leachate, were handled from 1976 to 1984. The landfill was repeatedly retrofitted in the 1970's and 80's with a leachate collection and gas extraction/air dike system to control leachate and gas migration. Prior to closure in 1984, OII was generating approximately 30,000 gallons of leachate per day which was recycled back into the working face of the fill. When solid waste to liquid ratios could no longer be achieved upon closure, leachate recycling was ceased; the leachate is currently being transported to a nearby facility for treatment. Estimates of gas generation range from 10-30 million cubic feet (mcf) per day with 4 mcf (of methane) being extracted by Getty Synthetic Fuels, for re-use. The remaining gas generated requires migration control via OII's extraction, air dike and flare system. The only other alleged barrier to contaminant migration is a naturally occurring siltstone layer underlying the western portion of the site including the hazardous waste liquid disposal area. Limited geotechnical data indicate that this layer varies in thickness and extent and may contain more permeable sand and gravel lenses.

Scoping and hazard evaluation activities revealed numerous deficiencies in landfill operation and design with potential impacts affecting groundwater, surface waters and air resources. Obvious symptoms of landfill mis-management included reoccurring on- and off-site leachate seepage and ponding, frequent intense odor episodes, slope failures and underground fires. Potential receptors identified included users of potable aquifers contained in two basins threatened by subsurface migration of leachate and those citizens residing in the vicinity (i.e., adjacent to) the landfill exposed to migrating gaseous emissions. An evaluation of surface water use in the vicinity of the site revealed no significant uses other than groundwater recharge. A workplan was subsequently developed that addressed further delineation of pathways and exposure to receptors with an emphasis on identifying any

immediate public health concerns. Specific tasks and objectives of data collection activities are presented below. All data generated as a result of field activities were collected and analyzed in accordance with specified quality assurance/quality control protocol to ensure the validity of data.

Community Well Sampling Program

Due to inadequacies in the leachate collection system and questions regarding the integrity of the siltstone layer as an effective barrier against migration, a community well inventory and sampling program was initiated to identify any immediate public health concerns. Data needed to develop a well inventory included:

- Location of all active public or private wells within a 1-mile radius,
- Water levels from wells within a 1-mile radius needed to develop flow gradients, and
- Well logs identifying lithologic sequence and well construction specifications including total depth, screened interval and seal design and depth.

Aquifers of concern were identified and defined as those aquifers that are of sufficient quantity and quality to be used extensively for drinking. Wells selected for sampling included all those wells within a 1-mile radius of the site which were screened in the aquifers of concern or were used to supply drinking water. Any wells that were identified as being screened in a zone potentially continuous with aquifers of concern were also selected for sampling. All samples were submitted for EPA priority pollutant analyses. Results of these analyses indicated non-detection for all volatile and semi-volatile parameters and background levels of all metals. These data served to allay public health concerns and were retained for comparative purposes as an indication of background water quality.

Leachate Characterization

Although the landfill had been retrofitted with a leachate collection system, surface leachate seepage areas occurred frequently on-site and in some areas off-site. Leachate characterization was conducted to identify contaminants of concern that may migrate via surface drainage and ponding to areas of groundwater recharge. Leachate characterization was also necessary to identify contaminants to be considered during the design of an on-site leachate treatment plant. Samples were collected over a 6 month period due to significant variations in leachate content. Samples were submitted for EPA priority pollutant analyses which revealed reoccurring contaminants including TCE,

TCA, PCE, vinyl chloride, benzene, toluene and lead. Sample locations were selected to obtain representative data on leachate generated from different areas of the landfill; locations included leachate storage tanks, leachate collection wells and on and off-site seepage areas. These data were used to assist in identifying locations of monitoring wells in recharge zones potentially affected by leachate migration and to target suspect contaminants for subsequent phases of the investigation.

Monitoring Well Installation

The next phase of the investigation involved the installation of six off-site monitoring wells. The landfill is located in an area situated between two major groundwater basins in southern California; hydrogeologic conditions underlying the site were not well characterized. Limited data from focused geotechnical studies, old oil and gas well logs and other regional hydrogeological reports were used to develop the monitoring well program. Due to the large area of the landfill, the initial wells were selected to monitor the hazardous waste liquid disposal area and those areas where chronic leachate seepage was documented. The objectives of the monitoring well program were as follows:

- To identify the location and vertical extent of underlying formations including aquifers of concern and aquitards,
- To evaluate the hydraulic properties of and continuity between saturated formations,
- To evaluate the elevation and location of formations underlying the site in relation to refuse zones, and
- To provide sampling points to monitor water quality adjacent to the landfill.

During drilling, all wells were lithologically logged and geophysical logs were completed on the open boreholes. Cores were selected from the siltstone for permeability testing to evaluate the effectiveness of this layer as a barrier to contaminant migration. Split spoon samples were also collected for priority pollutant analyses in areas potentially affected by leachate drainage to determine if infiltration was occurring. Short-term pump tests were conducted where aquifer conditions permitted. All samples collected from the completed wells were submitted for priority pollutant analyses; future sampling was scheduled to occur quarterly.

Results from this limited hydrogeological investigation were critical to developing a better understanding of subsurface conditions affecting contaminant transport. Hydrogeologic information obtained during drilling revealed that the siltstone contains significant water-

bearing sand and gravel zones exhibiting permeabilities much greater than noted in existing information. Although the areal extent and elevation of these zones in relation to the on-site hazardous waste liquid disposal area remains to be determined, their existence confirms the varying nature of the siltstone. Furthermore, analytical results from two of the six wells completed in an upper-most aquifer showed elevated levels of constituents previously identified in leachate samples including TCE, TCA, PCE, benzene, toluene and vinyl chloride. These data indicate that off-site migration is occurring and further implicate the inadequacy of naturally-occurring and engineered leachate control systems. Although contaminants were not identified in two wells screened in an aquifer of concern, information obtained on their vertical extent, hydraulic properties and continuity with overlying aquifers will be used to plan subsequent well installation phases.

Community Air Monitoring and Sampling

As a result of increasing odor complaints made by neighboring residents and elevated levels of vinyl chloride and methane detected in South Coast Air Quality Management District (SCAQMD) 24-hour air stations, a community air monitoring program was developed. The program was developed in coordination with an interagency committee comprised of state, local and federal agencies with the objective of assessing short-term immediate risks posed by methane and other select gas constituents in residential areas adjacent to OII.[1]

Specific protocol were developed which addressed the following:

- Interagency tasks,
- Community relations,
- Selection of a survey area including "control" homes,
- Survey and monitoring procedures for homes and gas probes,
- Field instrument uses and calibration,
- Action levels at which sample collection and/or evacuation would occur, and
- Analytical parameters and methodology.

Approximately 270 homes were identified for monitoring with an action level of 1,000 ppm methane specified to trigger sample collection, the action level for evacuation was set at 5,000 ppm methane.[2] Analytical parameters included methane, vinyl chloride, DCE, TCA, DCA, TCE, PCE, chloroform, carbon tetrachloride, benzene, toluene and chlorobenzene.

Survey instruments used included the OVA Model 108 and a Threshold Limit Valve (TLV) meter. These instruments were selected based on their low detection limits and sensivity to target compounds. Specific areas were selected at each house in order to monitor confined spaces where gases may accumulate and at the soil/foundation interface. Survey locations included:

- Water meter boxes,
- Along the outside perimeter of the foundation,
- Living/Family room,
- Fireplace,
- Underneath kitchen sink, and
- Underneath bathroom sink.

Since the levels of methane in homes exceeded the 1,000 ppm action level on only one occasion, 12 homes were randomly selected as sample locations. Samples were collected with evacuated flasks in an interior breathing zone. Contaminants identified at levels equal to or less than the laboratory detection limit (5 ppb) included TCA, benzene and toluene.

In addition to house-to-house surveys, 16 subsurface gas probes located in neighborhoods adjacent to the site were sampled. To ensure that the sample collected would be representative of the soil atmosphere in the vicinity of the probe terminus (depths ranging from 10'-40' below land surface), all probes were evacuated with a constant flow pump. A magnehelic gauge was used to monitor pressure in the probe to ensure that pressures did not exceed vacuum capabilities of evacuated flasks used for sampling. Analytical results of methane concentrations ranged from 0.000002% (2 ppm) to 100% methane. Target volatile compounds identified included vinyl chloride, DCE, benzene, TCE, toluene and chlorobenzene.

Data generated from the community air monitoring and sampling program were useful for a number of purposes. Results of house-to-house monitoring and sampling revealed detection level values of select volatile compounds while methane levels were significantly less than those found in gas probes and less than the action level specified for evacuation. Results from gas probe samples revealed significant methane concentrations in the majority of probes in addition to elevated levels of target compounds. These data suggest that off-site migration of gases is occurring in the unsaturated subsurface sediments. The gas probes will be resampled as the remedial investigation proceeds and will be used to design and monitor the effectiveness of an expanded gas collection system. House-to-house monitoring and sampling will also be rescheduled as necessary to identify any potential public health concerns.

SUMMARY

Development of an initial remedial investigation program for a landfill requires a thorough preliminary hazard evaluation to address immediate and long-term public health and environmental concerns. At Operating Industries, Inc. landfill initial data collection and field activities were focused to address immediate concerns while maintaining continuity with long-term objectives of the investigation. An assessment of contaminant sources, pathways and receptors assisted in defining the scope of work and limited the expenditure of unnecessary resources during

site characterization activities. While initial remedial measures were not deemed necessary based on data generated, results of this initial investigation served to identify areas of concern requiring further study.

REFERENCES

[1] Interagency members included representatives from U.S. Environmental Protection Agency, Los Angeles County Department of Health Services, California Department of Health Services and South Coast Air Quality Management District.

[2] The value represents 10% of the lower explosive limit (LEL) for methane which is approximately 5%.

RELATIONSHIPS BETWEEN LANDFILLED HAZARDOUS WASTE SAMPLE VOLUMES AND COMPOSITION DATA VARIABILITY

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INTRODUCTION

Various devices are commonly used in sampling wastes to evaluate their composition and hazardous properties, such devices including the thief and trier for sampling particulate wastes from waste piles (EPA, 1984). Readily available units may be used to sample granular solids having particle diameters of perhaps one centimeter or less. It is also sometimes acceptable to use an auger, scoop, or shovel to collect waste samples. Both the U.S. Environmental Protection Agency (EPA) and the California Department of Health Services (DHS) ordinarily approve of the use of corers, such as split-spoon and modified California samplers. These devices, which provide cores contained within cylindrical metal tubes, are especially useful where samples are to be collected at depth. The corer may be lowered through a hollow-stem auger and driven into the waste. The resulting samples tend to be relatively undisturbed, and volatile substances are retained within the cores pending chemical analysis, although there is some question about volatiles retention with this method of sampling.

Wastes collected with any such sampler may be subjected to chemical analysis. In the process, a sub-sample is usually taken by inserting a smaller corer or other implement into the waste to provide an appropriate volume of material for the kind of analysis to be performed.

Landfilled wastes consist mainly of particles of variable size, ranging from large blocks of concrete and household appliances, to bottles and bundles of newspaper, to fine-grained, decomposed household wastes and soil particles. Given that such materials have widely divergent compositions, the adequacy of such devices as the modified California sampler, providing sample volumes (core sizes) as small as 12 cubic inches, and the practice of sub-sampling may be reasonably questioned.

This paper addresses the issue of landfill sample volume effects on estimates of true waste composition, using a Monte Carlo approach. Two series of hypothetical waste volumes are generated with their associated

chemical compositions. The coring process is simulated and core compositions are also calculated. These are statistically examined and compared with the known compositions of the underlying hypothetical wastes, in order to evaluate sample volume effects on core composition distributions and variability.

METHODS

Computer System

All simulations in this study were run on an IBM-PC with accelerator and fully populated memory boards (640K). The programming language is FORTRAN-77.

General Model Design: Waste Synthesis

The model used in this study generates a one-yard cube of hypothetical waste ("sample support"). The sample support is subdivided into 46,656 1-inch cubes called "volume elements," these being considered internally uniform in terms of structure and composition. A given element can consist of any one of twenty categories of waste (e.g., glass, metal, soil), and each category, in turn, is composed of integral percentages of up to seven chemical species (e.g., carbon, lead, benzene, water) selected from among 100 possible.

The model generates wastes as discrete particles, each encompassing one or more elements of volume. The particles are randomly selected, one at a time, each in terms of its waste category, spatial orientation, size, composition, and position in the sample support. Each particle is constrained to represent one waste category (e.g., paper), but the percent composition is permitted to vary from volume element to volume element within the particle. The algorithm used allows the percent composition for a given chemical species and the composition ratios within a given volume element to be randomly assigned. Each percentage is considered to be drawn from an underlying normal distribution with associated mean and standard deviation provided as model inputs. The nominal percentage of each chemical species within any volume element is independently generated, these are summed over all species present in the element, and the percentages are then normalized so that they sum to 100.

Each waste category is specified in terms of the distribution characteristics of its largest particle dimension, which may be oriented along the vertical (z) axis or in the horizontal (x,y) plane, as well as in terms of aspect ratios for the two remaining mutually perpendicular axes. The direction of the longer of the two particle axes in the horizontal plane is randomized so that in approximately half the particles, it is aligned in the x-direction, and in the remainder, in the y-direction. Nominal particle percentages (e.g., 75% paper particles, 4% glass particles) are provided as inputs to the model. In addition, each waste category is characterized as being rigid (e.g., glass, metal) or conforming (e.g., rags, paper). Rigid wastes must fill the entire space they are selected to occupy. If part of that space has already been occupied by one or more particles previously positioned in the

sample support, then the model makes up to four more attempts to position the particle at other locations in the sample support. If all such attempts fail, then a new particle is randomly generated according to model inputs. In contrast, conforming waste particles fill the remaining voids of the spaces they are selected to occupy. Therefore, every particle of conforming waste selected is installed in the sample support.

The model distinguishes between matrix (assigned to one waste category) and non-matrix (the remaining 19 particulate waste categories). The model requires, as input, the percentage of the total sample support to be filled with non-matrix. The matrix material, which may be considered to represent soil, air, water, or other finely divided material or mixture, fills voids remaining after sufficient particles have been generated such that the percentage requirement for non-matrix has been met.

Finally, the model incorporates two random number generators. For generating uniformly distributed random numbers on the interval (0,1), a linear congruential random number generator is employed. Such generators can provide sequences of numbers that satisfy commonly used tests for distribution and independence properties (Yakowitz, 1977). The model uses the Box-Muller algorithm for converting uniform random variates, as provided by the linear congruential algorithm, to normally distributed random variates. The Box-Muller algorithm provides variates that can be shown to conform exactly to the normal distribution (Yakowitz, 1977).

General Model Design: Waste Sampling

The model simulates sampling with replacement. This is accomplished by simulated excision of undisturbed waste cores that are rectangular solids, the core axes being aligned with those of the sample support. The only input requirements for this purpose are the three spatial dimensions of the cores to be taken. In order to simulate sampling, the model first randomly generates decimal spatial coordinates, each on the interval (0,36) inches, and uses the resulting position as the lowest indexed corner of the core. The core then propagates along the three axes in the positive directions, and its composition is computed in terms of the chemical species of interest. Where the core propagates outside of the sample support along one or more axes, it simply "wraps around," re-entering the opposite side of the sample support along those axes.

General Model Design: Monte Carlo Simulation

The model may be configured in various ways to produce Monte Carlo simulations. For example, it can generate, and collect one sample from each of up to 50 realizations of the sample support based upon the input waste distribution properties and other data. It can also collect up to 50 samples from within one sample support. While these numbers of realizations are small compared to those commonly required in Monte Carlo simulations (where many thousands of realizations are sometimes generated), the model can nonetheless provide an indication of the effects of limited sample volume on inferred waste composition, and suggest further study in this area.

SIMULATIONS

Data Distribution Effects

For evaluating the hazardous properties of wastes, the EPA (1984) requires that sample composition data be subjected to statistical analysis based upon the t-statistic. The EPA (1984) discusses the importance of the normality assumption underlying the use of the tests it recommends, and suggests certain data transformations on the basis of relative magnitudes of the sample mean and variance for cases where the data appear to violate the normality assumption. The EPA (1984) also recognizes that the investigator frequently has relatively few observations with which to judge the validity of the normality assumption.

A related question revolves around the fact that waste composition data sometimes display a few high values (e.g., for lead or copper) embedded in a large number of observations in which the species is below detection limits. Such skewed distributions may be largely an effect of using sample volumes smaller than typical waste particle sizes. Alternatively, they may be a manifestation of localized waste deposits spatially removed from one another on a scale much larger than that of the majority of particles. In the latter case, the skewed distribution may be considered to characterize the waste as a whole rather than to characterize a few selected particles.

To examine data distribution issues, as well as for purposes of subsequent analysis in the present study, the model was configured to collect 50 samples of waste from a single sample support. Repeated runs were made with different sample volumes, and the data were examined, using the Kolmogorov-Smirnov (K-S) test (Ostle, 1963) for deviations from normality. In addition, the data were visually examined to evaluate distribution characteristics, and descriptive statistics were tabulated.

Effects on Data Variance

The variance of the simulated sample data for any chemical species consists of two components. One is due to the differences in composition from one cubic yard of simulated waste to another. The other component represents effects of sample volume, and is the one of interest here.

To generate the data required to address this issue, the model was set up to collect a single sample from each of ten waste sample supports, and a number of simulations were performed with different core sizes. For selected chemical species, the variances among samples and among sample supports were computed, along with the corresponding F-ratios.

Model Input Data and Conditions

Parameters required by the random number generator were tested by generating 40,000 random variates and examining them for uniformity of distribution and independence, the former with the chi-square goodness-of-fit test and the latter with the runs test. Once acceptable values were obtained, these were used for all subsequent simulations, changing only the seed values to provide the necessary number of sequences.

Municipal solid waste (MSW) particle size distribution data from Cambridge, Massachusetts, were adapted from Winkler and Wilson (1973), in order to develop geometric means and standard deviations for use with the model. Simulated cores were cubic with sides of 2, 4, 8, 16, 20, 24, and 28 inches. The resulting volumes ranged from 8 to 21,952 cubic inches, representing from .017 to 47.1 percent of the sample support.

Two separate series of simulations were run. In the first (Series 1), the distributions of particle lengths were as directly estimated from Winkler and Wilson (1973), and the hypothetical waste compositions were taken to be constant for each waste category. Hypothetical particle aspect ratios were also assigned, such that the simulated particle distributions resembled those of Winkler and Wilson (1973). The aspect ratios were also set with the long particle axis oriented in the x,y plane. The resulting model input conditions were also those used in simulations examining data distribution effects as described above.

In Series 2, while the general input conditions were similar to those used in Series 1, both the geometric mean particle sizes and the associated geometric standard deviations were reduced. The purpose was to obtain some indication of the sensitivity of results to such changes, although extensive sensitivity analyses were not performed in this study. In addition, non-zero standard deviations for waste category compositions were input to allow the composition of waste within a given particle to vary from one volume element to another.

Table 1 shows model inputs and conditions assumed in Series 1 simulations, and Table 2 provides composition data for five chemical species contained within the nine waste categories simulated. Tables 3 and 4 show the corresponding model input data for Series 2 simulations.

RESULTS AND DISCUSSION

The results presented here emphasize two waste species that are potentially important from a hazard evaluation standpoint (cellulose and lead), plus glass. The importance of lead is with respect to its toxicity and associated regulatory issues. Cellulose is a major constituent of paper, rags, and other wastes abundant in MSW. It is of interest here not only because of its abundance, but also because it is a major precursor for landfill methane formation and because solvents (e.g., benzene, trichloroethylene, contaminant-bearing water) may tend to associate with paper, rags, and other high-cellulose wastes. Glass, with particle and distribution characteristics different from the other two, is considered for purposes of perspective.

Figure 1 shows simulated particle length (largest dimension) distributions for paper, metal, glass, and total particles. Also shown, are the data extracted from Winkler and Wilson (1973), from which particle size distribution data were adapted.

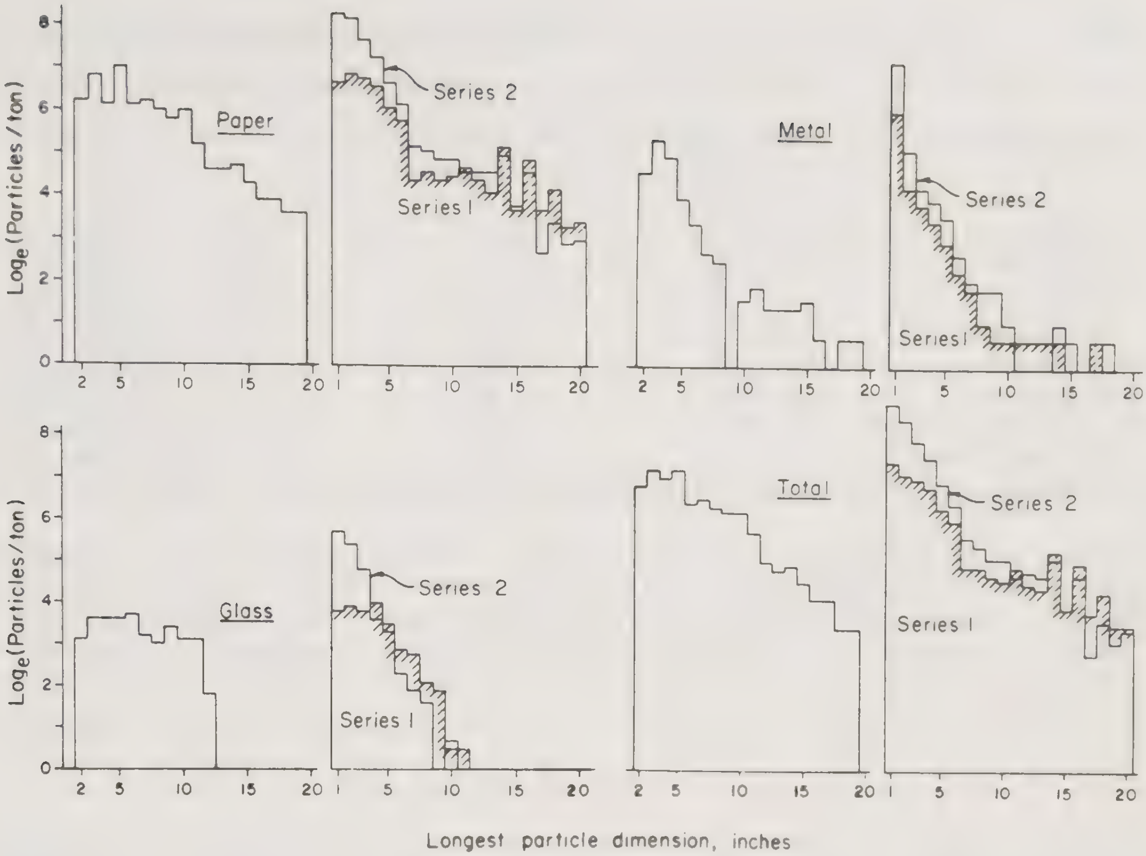

Figure 1. Particle frequency versus longest particle dimension. Each pair represents the data of Winkler and Wilson (1973) (left histogram) and simulated distributions obtained with simulation Series 1 and Series 2 input conditions (right histogram).

Sampling Data Distributions

Table 5 provides descriptive statistics obtained in examining core composition data distributions. It also shows results of the K-S test for deviations from normality at the 80% and 95% confidence levels. As indicated, no simulated core volume resulted in significant deviations from normality for cellulose. In contrast, the distributions of lead and glass concentrations deviated from normality in cores of up to 4096 cubic inches (2.4 cubic feet) and 64 cubic inches, respectively, at the 95% confidence level. At the 80% confidence level, deviations from normality were detected in cores of up to 8000 cubic inches (4.6 cubic feet) and 512 cubic inches for lead and glass, respectively,

Despite the fact that the distributions of cellulose (and that which might associate quantitatively with it) did not deviate from normality based on K-S, plotting showed the data to be skewed to the right. This

Table 1. Particle distribution parameters, Series 1 input conditions.

Waste Category	Geom. Mean ln(inches)	Geom. Std. Dev. ln(inches)	Particle %	A.R. x:y:z
1. Paper	1.70	0.60	75.0	1:.30:.05
2. Metal	1.36	1.46	8.5	1:.25:.10
3. Glass	1.79	0.51	4.0	1:.15:.10
4. Rigid plastic	1.09	0.41	2.0	1:.20:.10
5. Conform. plastic	2.02	0.64	6.0	1:.10:.10
6. Fabric	1.85	0.93	2.5	1:.20:.10
7. Food wastes	1.87	0.54	1.0	1:.20:.10
8. Heavy metal	0.10	0.05	1.0	1:.20:.10
9. Soil matrix (Represents 15% of sample support, others represent 85%.)				

Notes: Data estimated from Winkler and Wilson (1973). Particle sizes assumed to be log-normally distributed; "Geom. Mean" is the geometric mean, "Geom. Std. Dev." is the geometric standard deviation. "Fabric" is cloth, rubber, and leather. "A.R." is particle aspect ratio, orientation in x,y plane randomized; see text.

Table 2. Series 1 composition data inputs for the nine waste categories, in terms of five selected chemical species. Figures shown represent volumetric percentages within each waste category.

Waste Category	Volume Percentage of: Cellulose	Iron	Lead	Glass	Rubber	Other Major Species in Waste Category
1. Paper	50					Lignin, water
2. Metal		30	1			Al, Zn, Cu, Mg, Ni
3. Glass				20		80% Air
4. Rigid plstc.						Unspecified mixture
5. Conf. plstc.						Unspecified mixture
6. Fabric	40				10	Acrylic, water
7. Food wastes	10					Water, other food
8. Heavy metal			6			Zn, Cu, Ni, Cr
9. Soil matrix						85% Soil, 15% Water

Notes: Waste composition standard deviations set to zero. Percentage composition values are hypothetical. "Fabric" is cloth, rubber, and leather.

Table 3. Particle distribution parameters, Series 2 input conditions.

Waste Category	Geom. Mean ln(inches)	Geom. Std. Dev. ln(inches)	Particle %
1. Paper	1.35	0.50	75.0
2. Metal	1.15	1.35	8.5
3. Glass	1.40	0.45	4.0
4. Rigid plastic	1.05	0.35	2.0
5. Conforming plastic	1.70	0.60	6.0
6. Fabric	1.45	0.85	2.5
7. Food wastes	1.40	0.45	1.0
8. Heavy metal	0.10	0.05	1.0
9. Soil matrix (Represents 15% of sample support, others represent 85%.)			

Notes: Data modified after estimates from Winkler and Wilson (1973). Particle sizes assumed to be log-normally distributed; "Geom. Mean" is the geometric mean; "Geom. Std. Dev." is the geometric standard deviation. For particle aspect ratios, see Table 1. "Fabric" is cloth, rubber, and leather.

Table 4. Series 2 composition data inputs for the nine waste categories, in terms of five selected chemical species. Figures shown represent volumetric percentages within each waste category.

Waste Category	Volume Percentage (mean/std. dev.): Cellulose	Iron	Lead	Glass	Rubber	Other Major Species in Waste Category
1. Paper	50/10					Lignin, water
2. Metal		30/10	1/1			Al, Zn, Cu, Mg, Ni
3. Glass				20/20		Approx. 80% Air
4. Rigid plstc.						Unspecified mixture
5. Conf. plstc.						Unspecified mixture
6. Fabric	40/20				10/5	Acrylic, water
7. Food wastes	10/5					Water, other food
8. Heavy metal			6/5			Zn, Cu, Ni, Cr
9. Soil matrix						85% Soil, 15% Water

Notes: Waste composition percentages (means and standard deviations) are hypothetical. "Fabric" is cloth, rubber, and leather.

Table 5. Descriptive statistics obtained from simulated sampling data.

Species	Sample Volume (Cubic inches)	Mean (%)	Median (%)	Std.Dev. (%)	Minimum (%)	Maximum (%)	Zeros	K-S
Cellulose	8	36.93	38.54	10.82	0.88	50.00	0	
	64	36.37	38.40	6.90	17.84	47.65	0	
	512	34.67	35.76	4.58	20.59	42.30	0	
	4096	35.05	35.44	2.33	30.13	38.43	0	
	8000	35.32	35.67	1.57	32.44	38.30	0	
	13,824	35.37	35.43	1.08	32.92	37.32	0	
Lead	8	0.043		0.157	0.0	0.977	35	.05
	64	0.047		0.084	0.0	0.447	10	.05
	512	0.063		0.095	0.004	0.404	0	.05
	4096	0.052		0.044	0.015	0.146	0	.05
	8000	0.053		0.030	0.019	0.104	0	.20
	13,824	0.051		0.020	0.022	0.082	0	
Glass	8	0.156		0.456	0.0	1.919	43	.05
	64	0.223		0.406	0.0	1.683	25	.05
	512	0.316		0.312	0.0	1.788	2	.20
	4096	0.277		0.110	0.148	0.633	0	
	8000	0.276		0.079	0.175	0.490	0	
	13,824	0.272		0.062	0.184	0.423	0	

Notes: "Std. Dev." = standard deviation. Entries of ".05" and ".20" under "K-S" denote significant deviations from normality at the 95% and 80% confidence level, respectively, based on the Kolmogorov-Smirnov test. Sample support concentrations were cellulose = 35.53%, lead = 0.049%, and glass = 0.278%. "Zeros" = number of simulated zero concentrations.

also may be seen by comparing the means and medians in Table 5. With all cores simulated, but decreasingly with increasing core volume, the median exceeded the mean.

The lead and glass data were strongly skewed to the left with small sample volumes. As shown in Table 5, there were many zero concentration values for both species, with sample volumes of 8 and 64 cubic inches. The data also show maximum concentrations for lead in small cores that are as much as about 20-fold greater than the underlying sample support value.

Another manifestation of the effects of core size on data distributions was noted in a distinct bimodality of the lead concentration data. This can be attributed to the input data including two waste categories ("metal" and "heavy metal") containing lead at different concentrations. The bimodality was distinct for sample volumes as high as 8000 cubic

inches (4.6 cubic feet). Beyond that volume, a significant deviation from normality was not found (based on the K-S test), but evidence for bimodality still was visually noted in that the data distribution appeared platykurtic (flat-topped).

Data Variances

Figure 2 provides plots for both series of simulations, showing the effect of core volume on values of the F-ratio. The vertical dashed lines represent sample volume reference points, including the volume of a 2-inch diameter, 4-inch long, modified California sampler tube. The horizontal line on the figure delineates the region above which the core composition data variance statistically exceeds that of the sample support at the 95 percent confidence level [i.e., P(F<0.05)]. This means that for F-ratios plotted above the line, the probability of obtaining so large a ratio of the core variance to that of the sample support by chance alone, provided the underlying populations actually have the same variance, is less than 0.05. Accordingly, it can be concluded that taking core volumes of less than perhaps four cubic feet does significantly increase the variance of the resulting waste composition data in these simulations.

Table 5 shows that core data for lead and glass significantly deviate from normality, particularly for small core volumes. While the F-test does assume the data to be drawn from underlying normal distributions, it is robust to violations of this assumption, and the

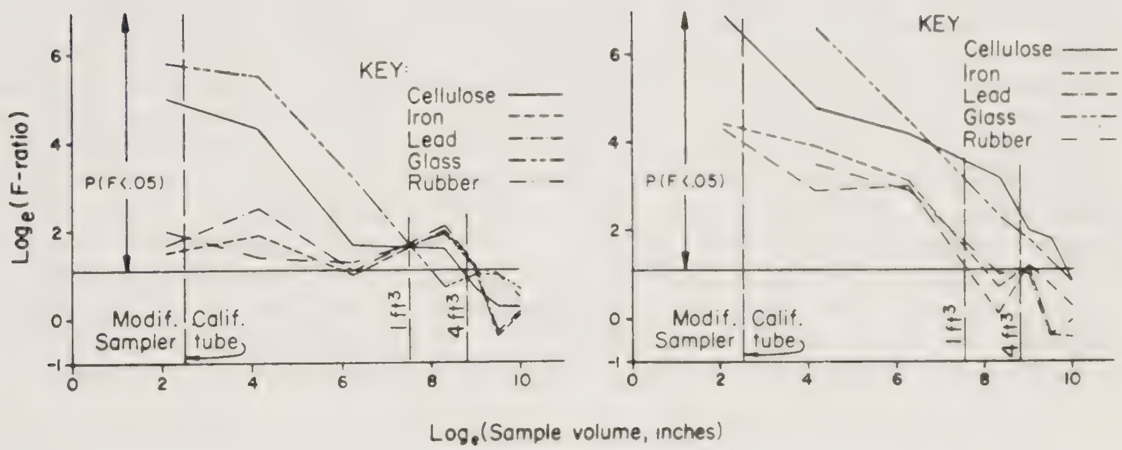

Figure 2. F-ratios obtained with Series 1 (left) and Series 2 (right) model inputs. Region above the horizontal line [P(F<.05)] represents statistically significant increases in core composition data resulting from the limited volume of sample collected.

assumption is of greatest consequence for F-ratios close to the critical value of F. The observed data generally deviate from normality most significantly where the F-ratios are much larger than the critical value. The results shown in Figure 2 can, therefore, be accepted despite some deviations from normality in the data for which certain of the variances were calculated.

Regulatory Implications

From a site investigation and regulatory standpoint, these results have a number of implications. While it can be argued that it is not necessary to increase sample volume, but simply to increase the number ("n") of small-volume samples in order to offset large variances, such an increase does not address the issue of non-normality. The t-statistic, and related computations recommended in EPA (1984) may not be appropriate for such metals as lead and other species present in rare particles unless large samples are analyzed. Results of the EP Toxicity test (EPA, 1984), in which such species as lead are extracted into a buffer, may exhibit similar strong deviations from normality. It can also be argued that increasing "n" may tend to increase sample acquisition costs (e.g., additional drilling), thus offsetting costs for increasing sample volume (e.g., use of a waste shredder/homogenizer). Shredding/homogenizing might be satisfactory, at least for non-volatiles analyses.

The present findings are also significant in terms of the provisions of California Administrative Code Title 22 (State of California, 1984), which incorporates SW-846 (EPA, 1984) sampling procedures, and includes regulations involving the TTLC (Total Threshold Limit Concentration) and STLC (Soluble Threshold Limit Concentration). The DHS sometimes accepts and interprets point estimates (i.e., individual sample values) of the TTLC and STLC for regulatory purposes. One effect of small sample volume is an increased probability of finding non-hazardous wastes to be hazardous (false positive) and hazardous wastes to be non-hazardous (false negative). For example, the TTLC for lead is 1000 ppm. Assuming an average specific gravity of 0.72 for the waste sampled, and with lead (assumed elemental) having a specific gravity of 11.3, the sample support lead concentration is about 7700 ppm. While this exceeds the TTLC nearly seven-fold, 35 observations out of 50 were less than the TTLC with a sample volume of eight cubic inches. The highest concentration was more than 150 times the TTLC. In contrast, with a sample volume of about 512 cubic inches, there was only one observation less than the TTLC, and the highest value was 63 times the TTLC. This better reflects the true condition of the sample support, and simulates only one false negative.

In conclusion, this study suggests that the analysis of small volumes of municipal solid waste (less than four cubic feet) introduces a number of potential problems in interpreting waste composition data. Specifically, the data tend to deviate from normality and to exhibit skewness. In general, for wastes representing a large particle percentage (>>50%), component concentration data are likely to be skewed to the right, while for components of rare particles, the data will tend to be skewed left.

Small sample volumes also yield chemical composition data exhibiting large variances that can be significantly reduced by using greater sample volumes. It appears that a desirable sample volume (smallest volume not resulting in a significant increase in data variance) may be on the order of 25-fold larger than the largest particles prevalent in the waste. Finally, limited sample volumes tend to yield multimodal distributions. As many modes may be observed for a given waste chemical species as there are distinct particle size classes containing that species.

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UNDERGROUND STORAGE TANKS

UNDERGROUND TANK MONITORING IN CALIFORNIA

THE MULTI-FACILITY DILEMMA

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INTRODUCTION

There are quite a few business concerns in California that have underground tanks at more than one facility and in more than a single regulatory jurisdiction. When an owner is faced with numerous underground tanks at many different sites, it is understandable that confusion exists. Often, owners of underground tanks are not nearly as well informed as they would like since monitoring technology and regulations have come into being in the past several months. The selection and implementation of the most appropriate monitoring system for each site is the owners' primary goal, a goal which is complicated by widely varying physical conditions and the uncertainty of newly enacted monitoring requirements.

The selection process must include an analysis of many parameters such as the physical setting, specific regulatory compliance factors and the costs of various monitoring alternatives. This paper discusses the factors involved in the selection process that must be considered by owners with many facilities prior to planning and implementation of an underground tank monitoring program.

PHYSICAL SETTING AT TANK SITES

Many different physical settings exist within the State of California. Underground tanks have been installed in areas of deep as well as shallow groundwater and in numerous different soil types. The physical setting very probably affects the monitoring alternative selected more than any other parameter.

Groundwater Conditions

Depth to groundwater and the direction of groundwater flow in the uppermost water bearing zones can be the most useful parameters which can be made available to the owner in the early stages of a tank monitoring system evaluation. Sources of data include local planning, building and health agencies, Regional Boards, State well log information, and other site specific data. Drawing on information obtained through past tank monitoring or contaminated site data in an area is often available and can be very useful. The usefulness of this data is related to the tank owners ability to accurately identify the number and location of wells which might be installed at the site. For example, if shallow groundwater wells are feasible as a monitoring alternative, lower costs would be incurred in both initial installation and long term monitoring. Lower costs may be realized primarily due to the absence or lack of a requirement for electronic-continuous monitoring equipment in the test borings/wells.

The direction of groundwater flow is important where only downgradient wells or test borings are required. Where wells are selected as an option, an accurate understanding of the groundwater flow parameters may mean a reduction in the number of wells installed.

Soils Factors

Virtually all types of soils have been excavated for the installation of tanks in the past. However, some soils can be more difficult to monitor for fuel or chemical leaks than others. Clayey soils can be far more restrictive to the passage of most vapors and liquids than are sandy soils. The immediate detection of a spill or leak in a well, however, can be much more difficult where clayey soils restrict vapor or liquid movement towards a detection point. Very loose soils or soils subject to severe changes in volume have been observed in the past to have created foundation failure and eventual leakage. Similarly, where tanks are located in high traffic areas, eventual compaction of the soils can lead to broken piping, crushed tank top or bottom, or other structural damage.

Drilling programs can be hampered by either very loose soils, very rocky formations, or large gravel or cobble deposits. It is not unusual for auger drilling activities to be stopped or delayed due to rock or gravels at a site. If alternate drilling methods are employed, sample acquisition, higher costs and other problems must be faced.

Occasionally, soils with high conductance and therefore higher corrosivity are identified at sites. Decreased tank life and failures or leaks are well known results of corroded tanks and

piping. Sites in the vicinity of San Francisco Bay, the Pacific Ocean and some highly saline lakes or desert areas in California can be expected to experience this problem.

Access and Proximity

Tanks that are covered by roofs, sheds or other permanent structures or that are in very congested areas can be difficult to monitor. Placement of wells or sensor controller boxes in a central location can be difficult as well. In addition, widely spaced tank areas can force many extra wells to be put in or more controller/sensor units to be installed. Tank removal can also be greatly complicated or made nearly impossible by physical obstructions. Drilling operations are often greatly complicated by difficult access and overhead obstructions. Operational requirements often must be considered when scheduling drilling or other on-site activities.

AVAILABLE MONITORING SYSTEM MEHTODS

Tank Monitoring Techniques

Each of the regulatory guidelines contain specific tank monitoring methods which must be employed by owners of underground tanks. Normally, a local jurisdiction will allow one of many options for implementation. Available monitoring features include:

- o groundwater monitoring wells
- o vadose wells/backfill wells
- o tank inventory device(in-tank sensors and controller)
- o continuous electronic monitoring sensors and controllers for wells
- o precision tank testing
- o pipeline leak detectors
- o chemical testing of soils, vapors and groundwater

Rather than conduct long-term monitoring utilizing one or more of the methods shown above, it is also possible to close and remove tanks as provided for in Sher Bill Alternative 8. Once removed, new tanks can be installed on site according to Sher Bill guidelines or fuel or other products can be derived from an off-site source.

Many vendors are currently available to supply the equipment or services described above and considerable developmental work is being done at this time in anticipation of the growing demand for tank monitoring devices.

Remedial Measures

When leaks or spills related to underground tanks are identified as a result of routine monitoring system installation, additional activities may be warranted besides those shown above. State of California Regional Water Quality Control Boards are often contacted at the appropriate stage of leak investigations for guidance on remedial requirements. A common approach is that precision tank testing is conducted first. If failing tests are derived, tank closure normally follows. Wells are typically drilled to determine the extent of the problem. If fuel or product is detected in the subsurface, no free product such as fuel is allowed to remain in groundwater resources, whereas, some fuel can remain in soils. Where solvents or other regulated substances are involved, a wide variety of agency responses are possible. Required activities may include groundwater pumping and treatment, soils hauling or aeration or other treatment, in-place remediation of soils by biodegradation or bio-enhancement methods, other aeration or carbon treatment technologies, or other methods as appropriate and techically feasible.

REGULATORY FACTORS

In California there are essentially three basic sets of regulations which govern underground tank monitoring programs. The Sher Bill technical reuglations, Subchapter 16, were formally approved in August of 1985 and are enforced in areas where no pre-existing local tank ordinance or statute is in effect. Another set of requirements are the guidelines for tank monitoring as applied in Santa Clara and Alameda Counties. These guidelines are enforced over much of the southern San Francisco Bay Area. In the Los Angeles County area, "Guidelines for the Underground Storage of Hazardous Materials" contain the applicable requirements. In most cases, alternatives are available to the tank owner in order to fit the monitoring system with widely variable physical settings and operational needs.

Sher Bill Regulations

In the Sher Bill regulations, there are eight tank test alternatives available to owners of underground storage tanks which contain hazardous or regulated substances. Only Alternative 1 contains no backup monitoring method of the long-term alternatives. The rest of the long-term alternatives require a primary and secondary monitoring method. Alternatives 7 and 8 accept reduced requirements for tanks which are small, are infrequently used, or will be removed within three years. The remaining alternatives, 2 through 6, include combinations of wells, daily monitoring or continuous monitoring equipment in wells, tank testing and other monitoring methods.

Depending on the tank owners need for inventory control, some in-tank leak detector and/or inventory control sensor may be feasible. This alternative (Sher Bill 5) requires other activities including annual precision tank tests, pipeline leak detection, and approved metering of fuel or product both in and out of the tank. Therefore, the cost to install this option should be carefully assessed in comparison to other alternatives, and evaluated against the perceived benefit of inventory control.

Santa Clara County Guidelines

Alternatives for tank monitoring in Santa Clara county are now quite similar to the State of California "Sher Bill" requirements with one notable difference. As used in Santa Clara and Alameda Counties, tank monitoring guidelines specify a precise formula by which the number and location of wells is selected. In general, where wells are selected in these counties, only one downgradient well is required per 35 lineal feet of tank dimension, regardless of the number of tanks present. Where groundwater is deeper than 20 feet, vadose zone wells (placed in the backfill) are also required, or may be installed in lieu of groundwater wells.

In some Santa Clara County jurisdictions, additional requirements may be imposed on tank owners such as precision tank testing initially, mandatory well installations, or other more stringent features.

Los Angeles County Guidelines

For sites located in Los Angeles County a specific monitoring program is required under guidelines enforced there. The following steps are expected to be utilized in Los Angeles County:

Step 1

- o preliminary geologic, hydrologic and soils evaluation
- o describe precision tank test method to be used
- o prepare plan of tanks, piping and boring locations
- o describe monitoring and inventory controls and sampling and analysis methods

Step 2

- o conduct test boring program to determine past unauthorized chemical releases
- o perform precision tank integrity testing
- o evaluate data generated and prepare technical report of activities conducted

Step 3

- o install monitoring devices in well borings/vapor wells
- o recommend additional control measures such as inventory system improvements, leak prevention devices on piping, groundwater wells, etc.

COMPARISON OF COSTS FOR INSTALLATION AND LONG TERM MONITORING

The final item in the monitoring alternative selection at multiple facilities is the costs involved in the initial installation and to monitor the system and the tanks in the long-term. All of the factors described above should be taken into account prior an evaluation of costs since it is likely some monitoring methods will be infeasible due to the physical setting or the operational requirements of a particular site. Simply choosing the least expensive method may not be serving the needs of every terminal or site in the company. At the same time, the monitoring program can be more confusing and difficult to manage if the monitoring methods selected for each terminal are far different from each other.

A significant cost to tank owners is the staff time required to manage tank monitoring programs. Someone in the facilities or maintenance group could become full-time if many sites are involved and if the monitoring system selected requires considerable routine reporting of results. Very often staff time costs are disregarded in calculating cost of these programs.

Consideration of the trade-offs between initial installation costs and long-term monitoring costs should be weighed carefully. For example, if continuous monitoring sensors are installed in wells instead of utilizing manual measurements daily, over many years, the reduced cost in staff labor can be significant. Yet, it is also true that an electronic system can be more expensive if it requires constant maintenance and calibration, or suffers breakdowns on a regular basis.

DEVELOPMENT OF THE MONITORING PROGRAM AT TYPICAL SITES

The optimum monitoring program is selected based on the factors identified above. The specific regulatory requirements, the physical factors at the site and the costs of various alternatives are weighed in making the final selection. We have selected three fairly common situations that are being faced by owners of multiple-facilities for discussion below. We have reviewed significant amounts of data to derive monitoring system plans for these clients. Results and a discussion of these projects are presented below.

Case Study 1

A freight trucking firm with headquarters in the San Francisco Bay Area has 15 terminals across the state and many more in the western United States. In this case, no in-tank inventory control was believed necessary by the client, primarily because the average age of the tanks is under 7 years and each terminal has a simple inventory system already in place. Fuel losses are simply not a problem for them. Monthly precision testing as an alternative was discarded due to the high cost. Øperationally, the tanks could not be removed. Due to the wide geographic distribution of the terminals, groundwater conditions were found to be as deep as about 200 feet and as shallow at a few feet.

A combination of monitoring programs have resulted for this client including one program using the Santa Clara County model, 9 terminals using Sher Bill Regulations, 2 of the Los Angeles County program, 2 terminals required no new monitoring due to double walled tanks, and one terminal will not be evaluated since it is a leased site. At the site with double walled tanks, continuous monitoring sensors will be needed between the primary and secondary containers. Several tanks are expected to be closed and removed in the near future. Normally tanks are removed because of age, known leaks or changed operational requirements. Also, due to the relatively young average age of the tanks, cathodic protection of some tanks may be recommended based on results of additional soils evaluations.

Øf the nine sites which come under the Sher Bill regulations, it was decided that Alternative 2 most closely meets the clients needs.

Case Study 2

A laundry and dry cleaning firm has 12 sites in California but only 9 have below ground storage of fuel or other regulated substances. At these 9 sites, as many as 50 tanks exist and of these, approximately 10 to 15 tanks contain or once contained solvents commonly used in the dry cleaning process. Many of the tanks are over 20 years old.

In formulating monitoring plans for these sites, not only were the physical setting and the regulatory environment explored, but some consideration was given to the removal of many of the older tanks prior to the installation of long-term monitoring systems. Due to the presence of solvent storage, the design of some monitoring wells and the soil and groundwater analyses will be adjusted accordingly. Some wells and test samples must accomodate the possible presence of both fuels and solvents in the monitoring - detection system.

Case Study 3

Another large trucking firm owns 16 sites in California and just recently purchased 7 more. Nationwide, the firm owns or operates approximately 500 terminals. Tank monitoring requirements are being addressed as they are received from the local jurisdictions. No overall preliminary evalaution was considered necessary by the client due to their in-house staff capabilities derived from past design and installation projects at fuel islands at their terminals. In a majority of the terminals, it is likely that Sher Bill Alternative 2 will be installed.

The newly purchased sites add considerable uncertainty in their efforts to monitor all underground tanks in their system. Complex legal agreements exist for these sites regarding responsibility for the cleanup of any soil and groundwater contamination which may have existed at the time of sale. Since considerable time may pass between the time the sale is made and the initial tank monitoring efforts are conducted, disputes could easily arise related to the timing of suspected or actual tank leak events. It is probable that initial precision tank testing will be conducted in each tank at the newly acquired terminals.

Another unique aspect of this firms tank monitoring effort is their desire to keep a centralized engineering staff in the midwest apprised of all developments. Considerable time, delay and expense may be incurred, particularly in the implementation phase, without instant access to an on-site representative of the tank owner. Unfamiliarity with tank testing procedures, local ordinances and local contracting practices also can lead to confusion and higher costs.

In summary, the key elements of deciding what to do for tank monitoring when you have many sites are:

- o understand the regulatory requirements in each area
- o acquire and evaluate data on soils, groundwater and uniques site conditions
- o carefully evaluate initial and long term costs of the various alternatives

Determining Appropriate Response for Underground Fuel Tank Leaks

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INTRODUCTION

Throughout California, many cities and counties with sensitive groundwater resources have already implemented ordinances that require monitoring of underground chemical storage tanks. The remaining cities or counties are in the process of implementing similar requirements in response to recently enacted state laws. Underground fuel tanks represent by far the largest number of the regulated underground tanks. Monitoring of these tanks will result in the discovery of hundreds, or more likely thousands, of sites where fuel contamination is present in soil or groundwater.

Many cities in the San Francisco Bay region preceded the State in requiring monitoring of underground storage tanks. That region has already been confronted with the task of responding to large numbers of underground fuel tank leak reports. The California Regional Water Quality Control Board, San Francisco Bay Region has developed formalized response procedures to provide a consistent and adequate preliminary response to these leak reports (1). The procedures are intended to provide a screening process to minimize additional follow-up where it is not required, and to insure such follow-up where it is necessary. These Guidelines are presently being implemented by the Regional Board staff in their responses to fuel leak reports. The Guidelines are also being considered as the starting point in the development of a statewide guidance document. A committee has been formed for this purpose, with representatives from many state agencies, under the initiative and direction of the Department of Health Services and the State Water Resources Control Board.

In drafting the Regional Board's Guidelines it was clear that there were several significant remaining issues. These issues could not be addressed in that document, because insufficient data was available or because they were outside the jurisdiction and control of the Regional Board. It was anticipated that these unresolved issues might detract from the utility of the Guidelines, and experience with implementation has, in fact, demonstrated the importance of these factors. The following are some of the issues:

- insufficient definition of the roles of various responsible regulatory agencies,

- insufficient actual field data to support <u>any</u> guidance numbers for water or soil,

- insufficient data management to refine or support the guidance numbers as new data is collected,

- absence of explicit instructions on application of site sensitivity assessment to evaluating the appropriateness of guidance numbers at a specific site,

- insufficient integration of the concerns of other regulatory agencies into the S.F Bay Regional Board's Guidelines,

- perceived conflict between the objectives of source removal (ie. excavation of old tanks) on the one hand, and detection and correction of existing contamination on the other,

- apparent lack of adequate regulatory staff to ensure application of the Guidelines to responses at all underground fuel tank leak sites,

The Guidelines are being used extensively in spite of all of the above issues. It is clear that each inhibits the implementation of the Guidelines to some extent. It is not clear to what extent the Regional Board will (or to what extent it can) resolve these issues. However, the committee that is developing a statewide guidance document has already acknowledged most of these issues and will at least attempt to address them in its work. In the interim, an understanding of the San Francisco Bay Region's approach, and of the issues that remain to be addressed may be useful to state and local regulators charged with responding to fuel tank leaks.

SAN FRANCISCO BAY REGION'S GUIDELINES

In the San Francisco Bay Region, a rapid increase in the number of reports of underground fuel tank leaks coincided with an increasing awareness of the vulnerability of groundwater to contamination from such leaks. A guidance document was developed for Regional Board staff to consult in determining the appropriate intial response, and the necessary adminstrative activites to insure adequate notification and documentation.

The procedure described in the Regional Board's Guidelines involves classification of fuel leak reports into several categories as shown in Table 1. The first category, defined as a "suspected leak" applies to a site where any one of the tank integrity indicators listed in Table 1 gives results indicative of tank leakage or fuel in adjacent soil. This category is intended to include any suspected, but unconfirmed, indication of leakage.

A site becomes a "confirmed release" site if it meets any of the criteria listed for that category in Table 1. These include a failed precision test (or pressure test for a pipe), an observed failure in a tank or piping, or significant loss of product as described in the table. Sites with a history of tank or piping failure that are located within 0.5 miles of a nuisance condition may also be classified in this category. When a "confirmed release" is identified, a subsurface investigation is required which consists of installation of at least one shallow monitoring well. Soil samples are collected at five foot intervals during the drilling. Although further characterization of soil contamination may be necessary after evaluation of the sampling results, the guidelines require that the boring be terminated at 45 foot depth if groundwater is not encountered. This investigation provides sampling, observation, and analysis of groundwater, if shallow groundwater is present. In all cases, it provides an indication

of the vertical distribution of contamination in soil below the tank.

The third category in Table 1 contains sites which are classified as "fuel leak cases". At these sites, the integrity indicators show a "confirmed release" and fuel contamination is found on or in the groundwater (see Table 1). Sites with a history of tank or piping failure or with fuel contamination in soil, or on or in groundwater may, at the discretion of the regulating agency, also be classified in this category. Remedial actions will be required at sites in this category. These actions will include removal and/or repair of the tank or piping and excavation of contaminated soil as appropriate to prevent the soil contamination from being a continuing source of discharge. The Guidelines indicate that, in most instances, excavation to less than 1000 ppm total hydrocarbons is necessary as part of initial site cleanup.

Removal of free product from the groundwater surface is also required in all cases if more than 1/4 inch of floating material is detected in an appropriately designed monitoring well or where lesser quantities contaminate or threaten to contaminate groundwater that is being used for domestic water supply. The Regional Board's Executive Officer must specifically approve any decision not to remove free product where more than 1/4 inch is detected in monitoring wells. Such approval is only considered in situations where potential impact on resources is clearly non-existant or where the cost of removal clearly does not bear a reasonable relationship to the value of the resource being protected.

Finally, the investigation at Fuel Leak Sites must, in all cases, include sampling and analysis of groundwater adjacent to the plume of free product to determine whether dissolved fuel components are present. Under the guidelines, if dissolved components are detected in groundwater, the severity is assessed using a relative-risk ranking methodology similar to that developed by Regional Board staff for the ranking of Santa Clara Valley groundwater contamination sites (2,3). Based on this evaluation the site may become a "Toxics Case", the fourth classification shown in Table 1.

Under the Guidelines, "Fuel cases" which become "toxics cases" are then handled consistently with other groundwater contamination cases regulated by the Regional Board. The responsible party is required to define the extent of contamination in soil and groundwater and to evaluate cleanup alternatives as outlined in the Regional Board staff's Guidelines for Establishing Cleanup Objectives(4,5). Based on that evaluation, a clean-up plan is then considered by the Regional Board in a Public Hearing.

Tracking of Fuel Leak Cases

In order to keep track of fuel leak reports, the Regional Board Guidelines specify two types of information be maintained for these sites. These include general information on the site (ie. address, operator, owner, contact person, reason for initial report, initial data on nature and concentrations of contaminants, etc.) and case tracking and status information (ie. a log of all reports of fuel leaks, staff assignment, screening determination, followup action, and reasons for action or for decision not to require action.) The Guidelines call for this basic information to be maintained in simple microcomputer databases for relatively easy manipulation and retrieval.

ISSUES IN IMPLEMENTATION

The procedures developed by the San Francisco Regional Board represent an attempt to define the decision-making process and the minimum information needs for making regulatory decisions regarding reports of suspected or confirmed underground releases of fuel. Application of the procedures has indicated that they can help to assure that responses are adequate for environmental protection and for assuring that remedial efforts are directed to meaningful investigation and effective cleanup at high-priority sites. However, the application of the Guidelines has also demonstrated the importance of continued efforts directed toward the resolution of the following issues which are not addressed in the Guidelines, and which affect its utility to some extent.

insufficient data to support guidance numbers

The Regional Board's Guidelines contain several numbers that represent concentrations or amounts of petroleum hydrocarbons which, when found at an underground fuel tank site trigger some requirement for further action (ie. installation of a monitoring well or extraction well). They also contain suggestions as to concentrations of contamination "almost always" unnacceptable in soil at an underground fuel tank leak site.

These numbers were not derived by technical consideration of toxicity, exposure potential, and estimation of environmental fate. Theoretical assessments of these factors yields uncertain results, at best, and such assessment can only be verified by comparison with a large amount of actual field data. Actual data correlating soil or free product contamination with groundwater contamination is essentially non-existent. Therefore, the numbers were developed empirically, using the Regional Board staff's observations of what is generally found at these sites. The intent was to require groundwater monitoring at all sites with relatively high concentrations of soil contamination, and not to require investigations at "average" facilities, which have contamination that is "typical" of the result of normal operation.

It is the Regional Board's intention to verify the guidance numbers by maintaining and compiling data on the outcomes of the investigations. The numbers could then be modified if the data indicated that modification was appropriate. For example, review of a year's data may indicate that lower concentrations in soil should trigger monitoring well installation (i.e., if all of the wells now required result in the discovery of major contamination), or it may show that the existing number never represents a problem (i.e., wells at sites with 100 ppm in soil do not result in the discovery of any significant contamination). In additon, it is becoming evident that a somewhat more sophisticated approach such as a "matrix" of guidance numbers, keyed to simple indicators of site sensitivity may be a more useful approach.

insufficient data management to refine or support the guidance numbers

Although it was intended that data management and data analysis would be used to verify the guidance numbers in the Regional Board Guidelines, there has been no such analysis to date. The Regional Board has not yet

computerized the data on sampling results. To the extent that the necessary data is available on paper in case files, it should be possible to use it for verifcation of guidance numbers, but with more difficulty than was anticipated in the Guidelines. However, a number of factors, including the increasingly decentralized nature of fuel leak response and understaffing at the Regional Board may result in inadequate data at the Regional Board for this type of evaluation. This evaluation was an integral part of the intent of these Guidelines, and is important to assure the validity and effectiveness of the Guidelines. It is therefore in the interest of both the regulators and the regulated community to see that this effort is pursued.

<u>absence of explicit instructions on application of site sensitivity assessment to evaluating the appropriateness of guidance numbers at a specific site</u>

The Guidelines specify minimum initial remedial actions that should be carried out immediately. Under the Guidelines, the risk to groundwater represented by dissolved contamination at a site is then ranked using a methodology similar to that developed for the Regional Board's "205j study" of groundwater contamination in Santa Clara County. Two issues have become apparent relative to this approach. The first is the Guidelines <u>perceived</u> requirement for one specified level of initial response (to soil contamination and free product), regardless of site sensitivity which may vary significantly from one location to another. The second is a lack of specific guidance on carrying out the specified risk assessment.

Regarding the first issue, the intent of the Guidelines was to provide guidance numbers which were relatively conservative as starting points for an engineer's evaluation of cleanup levels. The guidance numbers indicate a 100-fold range between "excavation to less than 1000 ppm" (total fuel hydrocarbons) in soil, which is "almost always necessary", and 10 ppm in soil, which is "almost never a problem". In practice it is becoming evident that engineering judgement is not being applied, either by the regulators or by the responsible parties. The 1000 ppm level is frequently being interpreted as a specified cleanup "standard", and then there is controversy as to its applicability to a specific site.

Considering the above, it appears that the implementation of the Guidelines would be improved if an explicit description is developed of the factors to be considered in selecting the soil concentration objectives for the intial remedial response. It would not be difficult to define a range of situations from contamination below the water table, in a drinking water aquifer, adjacent to wells, on the one hand, to contamination located far from any beneficial use or potential use of groundwater, on the other. Concentration levels for soil cleanup objectives from 10ppm (or lower) through 1000 ppm (or higher) could be assigned to appropriate points on the scale. Again, some form of "matrix" of guidance numbers adjusted for site sensitivity appears to be appropriate, and it appears that responsible regulatory agencies are likely to eventuall adopt such an approach.

Even with more explicit guidance on adjusting for site sensitivity, however, it is still necessary to stress the need for expert evaluation and professional judgement. The site owner is ultimately liable, for the cost of groundwater remediation if soil cleanup is insufficient, or for unnecessary cost if excessive cleanup is carried out in careless application of a

general guidance number to a specific situation.

Regarding the second isssue, evaluation of the degree of seriousness of contamination that remains after intial remediation, the "205j ranking methodology" is included only by reference in the document. Some modifications would be required for application of the existing methodology to fuel leaks, Also the necessary information groundwater resources and site sensitivity has not been compiled in a useable form for many areas. Therefore the staff that is implementing the Guidelines is using a significantly less detailed "interim" screening process to estimate seriousness of remaining groundwater contamination at fuel leak sites. Because the more detailed methodolgy is not being applied it is possible that the long-term requirements are not being determined, or they are not being determined adequately. As a result it is only the immediate remedial requirements at a site that are being resolved. for additional remedial work cannot be determined without some type of risk assessment relative to dissolved components.

<u>insufficient integration of the concerns of other regulatory agencies</u>

The San Francisco Regional Board's Guidelines were developed to assist its own staff in Responding to fuel leaks. An attempt was made to incorporate concerns of other responsible agencies. The document was circulated to those agencies specifically to identify and include such considerations. However, these issues were not well defined at the time, and at that time the agencies responses to the issues were yet to be formulated. The implementation of the guidance document has clearly defined some of the other agencies' issues and some progress is being made toward resolution of these issues.

Examples of "other agency issues" include offsite disposal of contaminated soil, which is regulated by the California Department of Health Services, air emmissions from cleanup operations, which are regulated by, the Bay Area Air Quality Management District, short-term threats to public health and safety from fumes (from residual contaminated soil or from cleanup operations), which are also the concern of the fire departments and the county health departments. In some instances the concerns of these agencies place constraints on the procedures specified in the Regional Board's Guidelines. The difficulty of resolution on a site-specific basis has been one major obstacle to achieving the standardization of case handling, and resulting efficiency of case handling and case resolution that were a primary purpose of the Guidelines.

<u>perceived conflict between source removal and detection of existing contamination</u>

The Regional Board Guidelines are fundamentally oriented toward the detection of existing contamination (by sampling soil and groundwater <u>outside</u> of the tank) and remediation wherever feasible. The local regulatory programs, and in fact also the State Board's Underground Tank Regulations, are apparently oriented more towards the prevention of future releases (by removing or integrity-testing old tanks, and providing double containment for new ones.) Concern has been expressed that the requirement for meaningful environmental sampling upon removal of existing tanks may discourage the removal of such tanks. It seems clear that the answer to this

objection is to require some form of "outside the tank" environmental sampling for all underground tank facilities. If that does not occur there will in fact be an incentive to maintain old tanks for as long as possible to avoid detecting existing contamination, particularly where the responsible party is aware of previous leaks which have been repaired.

apparent lack of adequate regulatory staff

The San Francisco Bay Regional Board is presently aware of 500 fuel leak sites in that region. Limited staff resources are allocated for regulation of fuel leak sites and application of the guidelines. The Guidelines were developed in anticipation of this type of situation, to streamline the response process and facilitate a "mass production" approach to the regulation of these sites. However, there has been no opportunity to establish the mechanics of that implementation. Also, the unresolved issues discussed in this paper have thus far prevented the Guidelines from resulting in the degree of standardization of response that was intended.

For the above reasons it is not possible to document a reasonable workload per staff member. Present staffing estimates are being based on the experience with handling of other types of groundwater contamination sites in the San Francisco Bay Area. The degree of savings in staff requirements that can be achieved under the guidelines is still an unresolved issue. However, existing staff is unable to even respond at an initial level to many of the reports that are received. The response function is transferred by default to the local regulatory agnecies, at least to the extent that they they are capable of, and interested in, assuming this role.

inadequate definition of the roles of responsible regulatory agencies

As noted, state agencies are presently unable to keep up with the workload generated by underground fuel tank leak cases, and many of the local agencies are becoming involved in regulation of remedial investigation and clean-up They are apparently assuming this role because their ongoing involvment with the faciiites at a local level makes them the most available and responsive regulatory entity. As noted previously, many other agencies have concerns which involve them to some extent in determining the appropriate response to an underground fuel tank leak.

The Regional Board's Guidelines represent an attempt to clearly outline the structure for decision-making and the procedures for response at these sites. However, even if all of the unresolved issues discussed here are resolved and included in a revised guidance document, the implementation of the document will not proceed smoothly until it is clearly identified which agency will perform each specific role in the procedure.

The most important need is for formal agreements between State agencies and local agencies as to the extent of local responsibilty in intial fuel leak response. The degree of responsibility may vary significantly from one jurisdiction to another, but it should be in writing and clearly understood. The most desirable approach to defining roles appears to be a through formal agreements, negotiated individually for each jurisdiction. An alternative approach would be state legislation, specifying a uniform role and providing a mechanism for funding the activities. In either case, the San Francisco Bay Region's Guidelines for Addressing Fuel Leaks, or an equivalent state-

wide document, could serve to focus the discussion on the specific responsibilities that are to be assumed by the respective agencies.

DEVELOPMENT OF A STATE-WIDE FUEL LEAK RESPONSE GUIDANCE DOCUMENT

At the state government level the need has been recognized for a consistent state-wide protocol for response to underground fuel tank leaks. It was also recognized that such protocols involve many responsible agencies, all of which should be involved in the development of the protocol, if possible.

To develop the state-wide response guidance document, a task force on Leaking Underground Fuel Tanks was established in late 1985 under the direction of the State Department of Health Services. This task force includes representatives from state and local public agencies with responsibilites related to the regulation of underground tanks and contamination clean-ups. Members of the task force include representatives of County Health departments, the State Department of Health Services, the State Water Resources Control Board and several Regional Water Quality Control Boards.

The purpose of the task force is to develop a document similar to the San Francisco Regional Board Guidelines discussed above, but based on a concensus sufficiently broad to make them applicable through out the state, and at several levels of government.

The product of the task force's work will be a guidance document acceptable to both the Department of Health Services and the State Water Resources Control Board for staff use in requiring or reviewing responses to underground fuel leaks. The document will also provide a clear statement of the state's concerns, to assist local agencies in understanding those concerns. In additon, the document will provide a structure that may help to focus the development of specific agreements on division of responsibilities at the local and regional levels.

The first drafts of the state-wide guidance document have been completed and are undergoing extensive internal review within the involved agencies. A draft for public review will be made available at the end of June. Public workshops will be held in late July.

To develop the state-wide guidance document, the Leaking Underground Fuel Tank Task Force has formed six subcommittees, each devoted to developing protocols or background information on particular aspects of underground fuel tank leak response. Included are subcommittees for Preliminary Site Assessment, Site Characterization, and Site Mitigation, each of which is to develop a protocol governing their specific phase of the response process. The other three subcommittees are concerned with Toxicology, Environmental Fate, and Quality Control/Quality Assurance. These will provide documentation that may be useful in risk assessment, and QA/QC procedures, to support the development of the protocols.

Based on the task force discussions to date and on the ealy drafts from several of the subcommittees, it appears that the state-wide guidance document will incorporate a preliminary screening methodology that includes a preliminary exposure assessment. The apparent potential for exposure will

be factored into the determination of whether additional investigation is required. Potential for exposure may also modify guidance numbers for determining short-term cleanup requirements.

When further investigation is required, the guidance document will most likely specify a methodology based to a large extent upon the Department of Health Services' "Site Mitigation Decision Tree" (6), perhaps with simplifications related to the similarity of many fuel leak sites. Regarding site mitigation, the document may outline the commonly available remedial alternatives and the expected efficiency of each. It will also probably identify the agencies responsible for establishing the requirements for mitigation. It is not yet clear to what extent the document will specify clean-up technologies or concentration limits for soil or groundwater.

PROSPECTS FOR RESOLVING MAJOR ISSUES IN FUEL LEAK RESPONSE

The activities of the Leaking Underground Fuel Tanks Task Force represent a significant opportunity for resolution of the issues identified above, which have limited the effectiveness of the San Francisco Bay Regional Board's "Guidelines for Addressing Fuel Leaks". Those same issues are being confronted by other agencies around the state, and they will also effect the "state-wide guidance document" if they are not adequately addressed in the development of that document.

The preliminary assessment subcommittee intends to include a simple preliminary evaluation of site sensitivity the preliminary assessment process. That would be a significant improvement, provided it does not result in a complicated and burdensome initial response procedure.

The subcommittees on Toxicology and Environmental Fate could provide either support for existing guidance numbers, or new numbers, depending upon their findings. Again, this work would benefit from the utilization of existing data, but the data is not yet in a compiled format and therefore is not readily available for that purpose.

The overall Task Force effort could significantly address the issue of overlapping responsibilities of multiple agencies. To the extent that the various agency representatives can define their agencies requirements for incorporation in the document, and to the extent that the document itself is internally consitent, the document can provide a single set of general procedures that are acceptable to all of the responsible agencies. A workable document could clearly identify the concerns, procedures, and general requirements of some of the agencies. However it is unlikely that a document could be applicable state-wide and also include sufficient detail to describe each of the wide range of inter-agency relationships that will exist. The details of inter-agency relationships will have to be handled by specific inter-agency agreements developed at a local or regional level.

In summary, the efforts underway to establish a state-wide guidance document will provide a useful starting point for discussing and organizing the activities of the many agencies involved in regulation of underground fuel tanks and underground fuel leaks. However, the application of the document can be expected to be constrained by many of the same factors that were identified in the development and implementation of a similar document at the San Francisco Regional Water Quality Control Board. The state-wide

effort may begin to address some of those issues, but it is unlikely that any of them will be adequately resolved in the state-wide guidance document. Therefore, the implementing agencies throughout the state should expect that they will have to confront many of the same problems in their own fuel leak response efforts.

ACKNOWLEDGEMENTS

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TABLE 1. FUEL LEAK SITE CATEGORIES AND SCREENING CRITERIA

CATEGORY - SUSPECTED LEAK

INDICATORS
- -inconclusive pressure test results (precision test tanks, pressure test pipes) or
- -Inventory loss over 3 month period ≥ 0.5% (of throughput for specific tank, or of sales for specific product if individual tank records are not available) or
- -Fuel vapors or free product of unknown origin within .25 miles or
- -Significant increase in vadose vapors

REQUIRED ACTION
- -Confirm by further testing of leak indicators

CATEGORY - CONFIRMED RELEASE

INDICATORS
- -Failed pressure test.
- -Inventory loss over 6 month period ≥ 0.5% (as defined above), or
- -Inventory loss over 3 months significantly ≥ 0.5%, or
- -Short-term loss indicative of catastrophic failure, or
- -Contaminated soil under tank ≥ 100 PPM total hydrocarbons, or
- -Observed hole in tank or piping

REQUIRED ACTION
- -Install monitoring well

CATEGORY - FUEL CASE

INDICATORS
- -Free product on groundwater and "Confirmed Release"
- or -Soil Contamination >1000 ppm total petroleum hydrocarbons

REQUIRED ACTION
- -Immediately abate any ongoing release
- -Excavate soil containing >1000 ppm Total Petroleum Hydrocarbons
- -Define extent of free product, Remove free product if >1/4 inch or if health threat or public nuisance.
- -sample adjacent groundwater for dissolved constituents.

CATEGORY - TOXICS CASE

INDICATOR
- -Dissolved contamination resulting in high relative risk ranking (205j ranking process)

REQUIRED ACTION
- After short-term remedial action (see Fuel Case, above) assign for handling as toxics case (define nature and extent of dissolved contamination, evaluate a range of cleanup alternatives and implement remedial action selected by Regional Board.

Note: from Ref.1, some indicators now defined by Subchapter 16 regulations

SELECTION CRITERIA FOR TANK MONITORING UNDER VARIOUS SITE CONDITIONS

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INTRODUCTION

The new California regulations for underground storage tanks allow several alternative monitoring methods for detecting leaks from new and existing tanks. In light of the constraints imposed by the new regulations, owners and operators of existing storage tanks must decide whether to keep, close, or replace their tanks. If tanks are to be kept, a monitoring strategy must be selected from among the available alternatives. Site-speciifc considerations will affect these decisions.

The decision to keep, close, or replace tanks should be made on the basis of an evaluation of costs, operating and maintenance constraints, and reliabilities. Before these factors can be compared for the options of keeping, closing, or replacing tanks, the monitoring strategy to be implemented if the tanks are to be kept must be identified.

MONITORING ALTERNATIVES FOR EXISTING TANKS

The State underground storage tank regulations are in the California Administrative Code, Title 23, Chapter 3, Subchapter 16. Article 4 of these regulations outlines the standards for monitoring existing tanks. Eight monitoring alternatives are described. They are:

1) Monthly Underground Storage Tank Testing.

2) Vapor or Other Vadose Zone Monitoring and Ground Water Monitoring with Soil Sampling.

3) Vadose Zone Monitoring, Soil Sampling, and Underground Storage Tank Testing.

4) Ground Water and Soil Testing.

5) Inventory Reconciliation, Underground Storage Tank Testing, and Pipeline Leak Detectors.

6) Inventory Reconciliation, Underground Storage Tank Testing, Pipeline Leak Detectors, Vadose Zone or Ground Water Monitoring, and Soil Testing.

7) Underground Storage Tank Gauging and Testing.

8) Interim Monitoring.

In addition, there can be County regulations that are more stringent than the State requirements.

TANK CLOSURE

Closure requirements for underground tanks are described in Article 7 of the State Underground Storage Tank Regulations. Tanks that are to be permanently taken out of service may be closed in place or removed. As with monitoring, more stringent County requirements can be imposed.

To remove a tank, the owner must:

- empty the tank;
- purge flammable vapors from the tank;
- demonstrate to the local agency that no unauthorized release has occurred (if feasible, soil samples should be analyzed);
- document to the local agency that the tank has been disposed of properly; or
- if appropriate, identify to the local agency the intended reuse of the tank; or
- if appropriate, identify to the local agency whether any part of a tank is to be reused as scrap material.

Where removal of a tank is not practical, the local agency may allow closure in place. To close a tank in place, the owner must:

- empty the tank;
- remove and dispose of associated piping, if possible; otherwise, empty and cap the piping;
- fill the tank with an inert solid, unless the tank is to be used for the storage of a nonhazardous substance;
- place a notice in the property deed with the tank's location, former contents, and closure method; and
- demonstrate to the local agency that no unauthorized

release has occurred (if feasible, soil samples should be analyzed).

TANK REPLACEMENT

The replacement of an underground storage tank requires all the actions described above for removing a tank plus compliance with the requirements of Article 3 of the State Underground Storage Tank Regulations regarding new tanks.

The requirements for the construction, installation, and monitoring of new underground storage tanks are extensive. For this discussion, only two major points need to be considered. First, there are two basic types of new tank installations that are allowed: double-walled tanks with the ability to monitor the space between the inner and outer walls of the tank, or single-walled tanks installed in a lined excavation with provisions for monitoring the space between the tank and the liner. Second, monitoring must either be by a continuous system with audible/visual alarms or by daily inspections.

SELECTING THE OPTIMAL STRATEGY

There are two steps in selecting the optimal strategy regarding existing underground storage tanks. First, the monitoring method to be used if the tanks are to be kept must be identified. This involves ruling out those monitoring alternatives that would not be allowed and selecting a preferred approach from the remaining alternatives. Next, the advantages and disadvantages must be compared between keeping, closing, or replacing the tanks. This involves evaluating the relative costs, operating constraints, and reliabilities of keeping, closing, or replacing the tanks.

Allowable Monitoring Alternatives

There are several key pieces of information that are needed to know which of the eight monitoring alternatives would be allowable for a given facility and to know how to implement some of the alternatives. These include:

- What is the depth to ground water?
    - less than 30 feet?
    - greater than 50 feet?
    - greater than 100 feet?

- Is there actual or potential beneficial use of the ground water?

- How many tanks are there?

- How close are the tanks to one another? Are they in the same or separate excavations?

- Is the material contained in the tanks motor fuel?

- Are the pipelines suction lines or pressurized?

- Is there any residual soil contamination ion the area that could affect vapor sensors in vadose zone monitoring wells?

Table 1 shows which alternatives may not be used under certain conditions.

Once the range of available alternatives is established their relative costs and operating requirements can be compared.

Monitoring System Costs and Constraints

The components and activities to be evaluated will include some or all of the following:

- Vadose zone wells for monitoring vapors in the unsaturated zone;

- Ground water wells;

- Continuous well monitoring devices;

- Continuous tank inventory monitoring devices;

- soil tests;

- Precision tank tests;

- Manual measurements of tank inventories; and

- Inspections of monitoring wells.

The costs for these items will depend heavily on site-specific conditions. Typical vadose zone well costs may be approximately $500 to $2,000 per well. Typical ground water well costs may be approximately $2,000 to $4,000 per well. The number of wells required varies based on criteria in the regulations. Soil sampling and analysis may cost approximately $200 to $500 per sample. Precision tank testing may cost approximately $300 to $500 per test. Continuous tank and well

monitoring devices may cost under $2,000 for a small installation or several thousand dollars for a large installation. Costs for manual measurements and inspections will depend on local labor rates.

Each monitoring system will require some combination of the above items. The preferred alternative will balance costs and convenience of operation.

Closure Costs and Constraints

The primary costs to remove a tank are associated with excavation and proper disposal of the tank. The primary costs for closing a tank in place are emptying the tank, removing or capping the piping, and filling the tank with inert solid material. In both cases, some additional expenditures are required for soil analyses to demonstrate that no significant releases have occurred.

Typical costs to remove tanks can vary from approximately $3,000 for a 500 gallon tank up to as much as $15,000 for a 10,000 gallon tank. Cramped work areas and long piping runs can add to the costs of removal. Closure in place costs would be lower; however, closure in place may not be allowed in some jurisdictions.

The most significant economic impact of closing a tank without replacing it may be the increased cost of obtaining the previously stored material by other means. Motor fuel costs can differ by twenty cents per gallon between bulk deliveries to an underground storage tank and purchases at a service station.

The importance of having a source of the stored material on-site must also be considered. In some cases, it may be essential to have on-site storage. In other cases, it may be almost as easy to obtain material from other nearby sources, such as fuel supplies from a service station.

Replacement Costs and Constraints

Installing new tanks can vary in cost from approximately $8,000 for a 1,000 gallon double-walled tank to approximately $30,000 for a 10,000 gallon double-walled tank. Additional costs can vary depending on how much associated piping there is and what type of secondary containment is used around the piping. Other costs may include continuous monitoring devices to detect material between the inner and outer walls of the tank or between the tank and the excavation liner.

- How many tanks are there?

- How close are the tanks to one another? Are they in the same or separate excavations?

- Is the material contained in the tanks motor fuel?

- Are the pipelines suction lines or pressurized?

- Is there any residual soil contamination ion the area that could affect vapor sensors in vadose zone monitoring wells?

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The components and activities to be evaluated will include some or all of the following:

- Vadose zone wells for monitoring vapors in the unsaturated zone;

- Ground water wells;

- Continuous well monitoring devices;

- Continuous tank inventory monitoring devices;

- soil tests;

- Precision tank tests;

- Manual measurements of tank inventories; and

- Inspections of monitoring wells.

The costs for these items will depend heavily on site-specific conditions. Typical vadose zone well costs may be approximately $500 to $2,000 per well. Typical ground water well costs may be approximately $2,000 to $4,000 per well. The number of wells required varies based on criteria in the regulations. Soil sampling and analysis may cost approximately $200 to $500 per sample. Precision tank testing may cost approximately $300 to $500 per test. Continuous tank and well

1) Motor Fuel Tanks at an Industrial Facility

An industrial facility maintains two underground tanks containing motor fuel for its vehicles. One tank has a capacity of 3,000 gallons; the other 2,000 gallons. The tanks are approximately ten years old. The average monthly fuel usage is 1,600 gallons. The depth to ground water in the vicinity of the tanks is estimated to be less than 10 feet.

Option I is to keep the tanks. A review of the monitoring alternatives listed in the regulations shows that alternatives 1, 2, 4, 5, 6, and 8 would be acceptable. Alternative 8 is quickly ruled out because it is only intended for tanks that will be closed within three years. The least expensive alternative is number 5. It is also the most convenient and reliable to implement.

Option II is to remove the tanks and obtain fuel from a nearby service station.

Option III is to replace the tanks with one new tank.

Table 2 shows the costs associated with the three options. Option I not only has a lower cost, but has the advantages of time savings since vehicles do not need to be taken off-site for fueling. It also affords protection against short term inconveniences should another "fuel crisis" occur in which fuel becomes difficult to obtain at service stations. The tanks' reliability is good since the tanks are only ten years old and they are expected to last beyond the next five years.

2) Solvent Tanks at an Industrial Facility

A manufacturing facility has five underground tanks containing a variety of solvents. Their sizes are 500, 1,000, 1,000, 2,000, and 4,000 gallons. The depth to groundwater is 70 feet. The ground water gradient is not precisely known. Three of the tanks were installed in one excavation. The other two tanks are in a second excavation. The tanks are approximately ten years old. The respective monthly throughputs are 100, 400, 500, 500, and 1,000 gallons.

Option I is to keep the tanks. Only monitoring alternatives 1 and 2 would be acceptable for this facility. Under alternative 2, three ground water wells would be required. Two vadose zone wells would be needed; one for each excavation. Continuous monitoring devices would be used in both the ground water and vadose zones wells.

Option II is to close the tanks. This option is not viable since the stored materials are needed every day in the manufacturing process.

Option III is to replace the tanks with four new tanks (the contents of two of the existing can be held by one new tank).

Table 3 shows the costs associated with the three options. Option I has a lower cost. Since the monitoring devices that would be used in either Option I or Option III are similar, their operating and maintenance requirements are similar with perhaps less time being required for Option III. The reliability of new tanks with built-in provisions for monitoring is a little better than vadose zone and ground water monitoring wells. Releases from a new tank would presumably be detected before the material escaped from the secondary containment. Releases from an existing tank could contaminate a small amount of soil and ground water before detection.

If the local environmental conditions are very sensitive, it could be worthwhile to replace the tanks. In the event of a small release from the existing tanks, the amount of contamination that could occur before detection could still result in cleanup costs that would be higher than the costs of new tanks.

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* * *

TABLE 1

CONDITIONS INFLUENCING WHICH MONITORING ALTERNATIVES MAY NOT BE USED

Conditions	Alternatives 1	2	3	4	5	6	7	8
Ground water depth less than 100 feet and has actual or potential beneficial use or is hydraulically connected to such water			x					
Ground water depth greater than 30 feet				x				
Tank contents non-motor fuel					x	x		
Ground water has actual or potential beneficial use or is hydraulically connected to such water				x				
Frequent inputs/withdrawals							x	
Tank will not be removed in the next three years								x

TABLE 2

EXAMPLE 1: MOTOR FUEL TANKS AT AN INDUSTRIAL FACILITY

Based on five years of operations

Option I: Keep tanks.

Permit fees	$552
Precision tank tests	$750
Upgrade pumps and meters	$2,000
Tests at 12, 24, 36, and 48 months	$3,000
Assume 4 hours/week for inventory reconciliation at $10/hour	$10,400
	$16,702

Option II: Remove tanks.

Permit fees	$150
Tank excavation	$7,000
Tank disposal	$1,700
Soil/water sampling	$50
Analyses	$300
Assume fuel cost differential of $0.20/gallon for 1,600 gallons/month for 60 months	$19,200
	$28,400

Option III: Replace tanks.

Permit fees	$376
One new tank	$15,000
Assume 2 hours/week for inspecting/maintaining monitoring system at $10/hour	$5,200
	$20,576

TABLE 3

EXAMPLE 2: SOLVENT TANKS AT AN INDUSTRIAL FACILITY

Based on five years of operations

Option I: Keep tanks.

Permit fees	$1,080
Ground water wells (3)	$9,000
Vadose zone wells (2)	$2,000
Monitoring devices	$5,000
Assume 4 hours/week for inspecting/maintaining monitoring system at $10/hour	$10,400
	$27,480

Option II: Remove tanks.

(not considered)

Option III: Replace tanks.

Permit fees	$1,080
New tanks (4)	$43,000
Monitoring devices	$3,000
Assume 2 hours/week for inspecting/maintaining monitoring system at $10/hour	$5,200
	$52,280

RECENT DEVELOPMENTS IN UNDERGROUND STORAGE TANK MONITORING TECHNOLOGY

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Protection of groundwater from leaking underground storage tanks has been a growing public concern that has resulted in an increasing number of state and local governments adopting laws and regulations to control the underground storage of hazardous substances. The federal government, recognizing the problem, has included provisions in the 1984 Amendments to the Resource Conservation and Recovery Acts (RCRA) to regulate underground storage tanks.

In August 1985, the State of California adopted regulations and standards for underground storage tanks including alternatives for monitoring existing tanks. These regulations which were mandated by state law are to be enforced by local agencies through permit programs. Local jurisdictions that adopted their own ordinances before January 1, 1984 are exempt and can enforce their own requirements and regulations. To date there are 54 county agencies and 48 city and local fire departments in California enforcing underground tank regulations. Of these local agencies, more than half are exempt from the provisions of state regulations.

The number of enforcement agencies and increased regulatory requirements have resulted in a confusing array of monitoring techniques and technology to comply with these regulations. This is particularly significant to the petroleum industry and companies with facilities in several local jurisdictions. In California, nearly 120,000 registered underground tanks are used for motor vehicle fuel storage--that represents about 70 percent of total registered tanks.

This paper focuses on current technology and techniques available for monitoring existing underground tanks used for motor vehicle fuel and related petroleum products. In particular, the applicability and effectiveness of these techniques to detect hydrocarbon leaks and comply with state and local regulations will be discussed. Emerging technologies currently under development to monitor existing underground tanks will be reviewed.

INTRODUCTION

Prevention of leaks, spills and overfills of petroleum products from underground storage systems should be given a high priority to properly protect the environment and valuable groundwater resources. Underground leaks, particularly those minor and moderate ones that go undetected for years, are not only costly but more importantly, environmentally damaging.

There are several accepted practices and construction standards which when implemented and followed properly could reduce the risk of leaks and spills and prevent any associated environmental damages. Among these are:

1. Proper installation practices and adherence to accepted construction standards.

2. Selection of proper materials such as cathodically protected steel tanks, double walled tanks, and corrosion resistant tanks.

3. Proper inventory and stock controls.

4. Leak detection and monitoring systems.

5. Conscientious maintenance and housekeeping practices.

Many of the reported incidents were due to careless and sloppy housekeeping and poor maintenance practices. The lack of monitoring and enforcement of required maintenance practices and inventory control have also contributed to leak occurrences.

Inventory control, properly done and accurately maintained form the first line of defense in early detection of product leakage. However, there exists a lack of understanding on the part of the underground tank owners and operators as to the cost and environmental consequences of leaking hazardous materials. As one State regulator stated: "Current state and local regulations on underground storage tanks would not have been necessary if only the operators and owners of these tanks had used proper inventory control procedures in detecting leaks before it affected the groundwater and became a catastrophe."

LEAK MONITORING TECHNIQUES

Leak detection and monitoring systems became a regulatory requirement to ensure redundancy and increased reliability in protecting groundwater and the environment. Current techniques for leak monitoring can be classified into three basic categories:

1. Tank testing methods to test tightness and integrity of tanks.

2. In-tank monitoring or internal detectors to monitor levels.
3. External monitoring systems placed outside the tanks.

There are several technologies available or under development in each of these categories. A brief discussion of these available technologies is presented.

Tank Testing Technology

Tank testing has been an accepted practice in the petroleum industry to determine underground tank leaks. The standard procedures and specifications are defined in the National Fire Protection Association (NFPA) publication 329 titled "Underground Leakage of Flammable and Combustible Liquid."

The basic criteria of tank testing is to detect leaks in or out of tanks as small as 0.05 gallon/hour. The test method must take into account the following to be acceptable:

1. Product temperature stratification
2. Trapped vapor or air pockets
3. Evaporation
4. Tank end deflection
5. Thermal expansion or contraction
6. Pressure variations

Because of these many variables, leak detection to this level is difficult to accomplish particularly in short-term tests.

Petro-Tite Test or Stand-Pipe Method. This test method is based on the principle of applying a hydraulic pressure head to the tank by means of an externally connected stand-pipe. Product is continually circulated to stabilize the temperature while the temperature measurements are taken with a thermistor probe. Product level in the standpipe is continually monitored for rise or fall and measured amounts of product are added or removed. Calculations are then made to relate product volume change versus temperature to determine leak rate.

Leak-Lokator or Bouyancy Method. Originally developed by Sun Oil Company, the Leak-Lokator is based on the principle of bouyancy. Leakage is measured by sensing weight changes in a sensor suspended in the liquid of the tank. Any change in liquid level above the sensor will alter the bouyancy force and weight of the sensor. This change is measured by an analytical balance which is connected to a strip chart to record any changes. The test is calibrated by adding a known small amount of product at the start of the test and recording the change. Temperature changes are monitored in the center of the tank for use in estimating the effect of thermal expansion or contraction on volume change.

Ezy-Check or Pressure Measuring Method. With this method, air bubbles are injected 3 or 4 inches below the liquid surface of the tank while pressure is being monitored at this point. Pressure readings are recorded and when a change occurs, liquid is either added or removed until the original reading is attained. Temperature is recorded for use in estimating thermal effects in volume change. The test can be done at different liquid levels to determine if the leak is in the product lines, or in the tank.

Associated Environmental System (AES) or Mass Weight Method. The AES tank testing method is based on measurement of mass weight. Using state-of-the-art electronics and computer technology, an in-tank sensor (mass weight transducer) and RTD temperature probe are inserted into the fill opening to monitor the change in mass weight. The sensor and temperature probe are connected to a computer to record the measurements and visually display the data on the monitor screen. It then provides instantaneous printed results of both graphs and data. Because of its simplicity and ease of use, it provides minimum disruption and downtime of the facility.

Sonar Method or Vacutect. This method, originally developed by Athabasca Research Ltd., used a hydrophone and pressure sensor inserted into the tank and connected to a microprocessor. The internal pressure of the tank is then incrementally reduced. If there is a leak, the reduced pressure will cause the ingress of air and formation of bubbles. The bubbles are detected by the hydrophone and have characteristics which permit identification of the size, and approximate position of the hole in the tank. Anomalous situations such as ingress of water because of high water tables are addressed by auxiliary sensors which detect and measure the ingress of water. The system reportedly can detect and locate holes as small as 1/4000 inch diameter but is not capable of estimating leak rates.

Helium Test Method. Also known as the Smith and Denison System, this method is based on the principle of sealing all tank openings and then pressurizing the empty tank and piping to a maximum of 0.5 psi using helium gas. Helium, being a relatively small and mobile molecule, can readily pass through any holes in the tank. A detector, connected to a portable mass spectrometer, is then used to search for helium above the tank and piping. Small holes on 4-foot centers are bored on the ground above the tank to determine the approximate location of the leak. This test can take up to several hours, and in some cases, overnight observation is necessary.

Laser Beam Detector. Funded by the American Petroleum Institute, a research program was conducted to determine the feasibility of using a laser system to detect the change in the level of products in tanks. The system consists of a laser measurement system, two long brass tubes, an aluminum float with an internal cube-corner reflection, a temperature measurement system, and a data acquisition microprocessor. Research

findings indicate that although the method is feasible, its detection accuracy is only 0.1 gallon/hour which is less sensitive than the NFPA requirement of 0.05 gallon/hour. This method has not been developed commercially.

Shell Canada System. This method is a new concept developed by Shell Canada and is currently under field evaluation. The system is based on magnification of liquid level change due to tank leakage by isolating the tank from the atmosphere, except for a 1-inch pipe inserted into the tank's fill opening. The pipe extends from above the top of the fill opening to about 6 inches off the tank bottom. The tank has previously been filled to minimize the void space. The pressure in the void at the start of the test is equal to atmospheric pressure. Should the size of the void increase due to product loss, the pressure in the void will decrease in accordance with standard pressure, volume and temperature relationships. Any changes in pressure is then reflected in the change in liquid level in the insert pipe. The commercial use of this system is being studied by a task force of the Petroleum Association for Conservation of the Canadian Environment (PACE).

Capacitance Probe or Mooney Tank Leak Detector. Mooney Equipment Company introduced a capacitance probe that reportedly can measure level changes in the tank of 0.01 to 0.02 inches and detection accuracy of 0.02 gallon/hour. The system is being tested and no results are available at this time. The system is based on the principle that a buoyant member floating on the product will experience a change in elevation as product level changes in the tank. This change is measured by an indicator connected to a buoyant member. Temperature is measured to account for thermal effects. Calibration is done by adding and removing a measured amount of product and the elevation change is noted.

Arco Underground Tank Test. Developed by Arco, the system is based on measuring the position of a float over a period of time and then relating to volume changes using a calibration technique. The position of the float immersed in a liquid relative to a fixed point will vary as the liquid level changes. A photo optic device is used to sense the movement of the vertical float and is capable of measuring changes in liquid level on the order of five microns. Although commercially available, it has not been widely accepted by regulatory agencies because it can only test up to 80 percent full tank.

Hydrostatic Test. There are many variations or versions of this test but, basically, all consist of filling the tank with product and applying hydrostatic pressure with a hand pump, standpipe or other device. Reduction in pressure signifies a leak with a measured product added to repressure the structure. This then is related to some temperature measurement to compensate for thermal effect in confirming the leak. The test is normally not precise enough to detect small leak rates as defined by NFPA 329.

In-Tank Monitoring Techniques

In-tank or tank level monitoring is essentially based on the principle of inventory reconciliation and stock control in combination with tank testing technology. Techniques currently available range from manual gauge sticks to computerized tank level monitors with state-of-the-art electronics.

Although inventory reconciliation has some associated problems, it can be the first indicator of leak when done properly and accurately. Most of the common problems and sources of error in inventory control that could lead to false alarms are:

1. Discrepancies in delivery measurement

2. Inaccurate pump meters

3. Theft

4. Evaporation

5. Improper record keeping

6. Precision and accuracy of measurement

Manual Gauging Method. This method of in-tank monitoring and inventory reconciliation to detect leaks and product loss is a standard procedure in the petroleum industry but has not been properly enforced and accurately done. Gauge or dip sticks have been standard instruments in measuring volume of product in the tank. There are manual gauges available now that can also measure depth of water at the tank bottom.

A recent development in manual gauges is a battery-operated liquid-level tape that can measure product level, temperature and water level. It is intrinsically safe with LCD readout of information as well as an audible tone if water is encountered. The probe allows readings to within 3/8-inch of the bottom of a tank.

With manual gauging, only major discrepancies become apparent and small leaks may not be identified. There are also several sources for error that must be carefully accounted for, such as accuracy of level reading and errors in arithmetic. Because of these practical problems, stock variations are based on deviations from normal allowances to indicate a possible leak or product loss.

Automated Tank Gauging Systems or Tank Level Sensors. In order to compensate or eliminate some of the problems and sources of errors associated with manual gauging, a number of microprocessor-based systems have been developed. These tank level sensing or gauging systems are designed to improve inventory management and detect leaks, even small

ones, through continuous-level monitoring and tracking of product throughput and input.

Automated systems currently available will monitor tank levels continuously as well as:

1. Automatically verify fuel deliveries with printouts of volume and temperature.

2. Measure and record depth of fuel and water.

3. Calculate volumes with temperature compensation.

4. Programmable alarms for overfill, sudden loss, low inventory, or high water.

In addition, these automated systems have capability to do leak detect mode and reports. This allows the operator to do leak detection year-round at his convenience. A leak alarm is triggered if the system detects a loss of product above the trigger amount. The reported sensitivity of the system for leak detection is 0.2 gallon/hour.

Three of the systems available commercially are:

1. Veeder-Root Tank Level Sensor. Operates based on a capacitance principle to sense liquid level with temperature compensation.

2. Gilbarco Tank Monitor. Combines two technologies; micro-processor electronics and ultrasonic measurement.

3. AES In-Tank Constant Monitor. Uses a mass weight transducer and RTD for temperature measurement combined with state-of-the-art electronics and computer technology.

In 1981, PACE conducted a research project to develop a device for positive and rapid detection of leaks in underground tank systems. A prototype unit was developed and tested in the laboratory as well as in the field. The accuracy of the unit is sufficient to measure tank volume changes in the range it was designed for. The study, however, concluded that there are sufficient grounds to suggest that it is impossible to design an apparatus to measure leak rate in magnitude of 0.05 gallon/hour through volume change in 15- to 30-minute time intervals because of ground- and tank-related effects that cannot be isolated or corrected. Factors such as the nature of soil mechanics, random ground motion due to external sources, and expansion characteristics of trapped air, have all shown greater effect on the accuracy of leak detection and measurement than originally expected.

External Tank Monitoring Techniques

The other group or classification of leak detection systems is external tank monitoring, using either periodic or continuous surveillance of leak or spill. External tank monitoring requires the use of observation wells or probes installed close to the tank excavation area to detect a leak as early as possible. The wells are used as leak detection systems by monitoring either the groundwater or vapor for the presence of hydrocarbons using portable or continuous sensing devices.

Groundwater Monitoring. Groundwater monitoring wells as the primary means of leak detection are not recommended in areas where groundwater has beneficial use or is a primary source of water supply. It can be used, however, in areas where groundwater is of no beneficial use and is present within the tank excavation. If used for leak detection, groundwater observation or monitoring wells should be installed within the tank backfill as close to the tanks as possible to be most effective.

The design and installation of observation wells are similar to that of a monitoring well using a minimum 2-inch, schedule 40 PVC pipe. The depth of the wells should at least extend to the bottom of the tank excavation, although some agencies may have different requirements. Groundwater monitoring wells placed outside the tank backfill or in deep water table conditions could fail to provide early detection since it will require considerable time and amount of hydrocarbon to leak before it could be detected.

Leak detection devices or sensors available for use in monitoring hydrocarbons in groundwater include:

- Grab Samplers - This device is a clear plastic bailer with a ball valve in the bottom to collect groundwater samples. The sample is visually inspected for presence of free floating product as a layer or film.

- Chemical Indicator - This is a hydrocarbon sensitive paste that changes color if product is present in the groundwater. A thin film of paste is placed on a clean rod before it is lowered into the well.

- Interface Probes - This probe uses an optical sensor to determine if the liquid level is reached and a conductivity sensor if liquid is water or oil. A precise determination of the air/oil/water interface can then be obtained.

- Product Soluble Sensors - A styrene-butadiene copolymer resin sensor is connected to a spring-loaded indicator and placed in a monitoring well. Any product present in the groundwater

will dissolve the sensor element and release the weight, signaling an alarm condition.

- Thermal Conductivity Sensors - A floating probe that measures the thermal conductivity of liquid at the air/liquid interface is placed in the well. When a nonpolar fluid such as hydrocarbon is detected, an alarm signal goes on.

- Product Permeable Sensors - These sensors which are both hydrophobic (water repellant) and oleophilic (permeable to hydrocarbons) materials have been used for leak detection. The two types of construction of this sensor are the braided cables using this material as insulator and the perforated polyethylene tubing coated with the material.

- Electrical Resistivity Device - A monitor circuit continuously reads a 100 K ohm resistor. A drop in resistance due to a short or a break causes an alarm condition. The sensor cable is a conductor insulated by a styrene-butadiene copolymer which dissolves if liquid hydrocarbon is present in the groundwater.

Vapor Monitoring. Observation wells or probes can be used to detect leaks by monitoring the presence of hydrocarbon in the vapors in unsaturated zone. Due to the high volatility of hydrocarbon, vapors migrate more rapidly particularly in porous materials.

Like groundwater monitoring wells, vapor wells or probes should be installed within the tank backfill as close to the tank as possible for early detection. These probes are typically smaller diameter pipes, 1/2 to 1 inch in diameter, with depths extending to the bottom of the tank backfill excavation. The slotted portion should extend almost to the entire depth of probe to ensure that the slots remain exposed above the level of the water table at all times.

Leak detection devices available for monitoring hydrocarbon vapors can generally be classified as either passive or aspirating devices. These devices can also either be portable or continuous monitoring systems complete audible alarm and data storage. Among the commercially available leak detection devices are:

- Detector Tubes - These are chemically filled tubes that are used to test for specific compounds. Vapor samples are aspirated from the probe into the tube with an air pumps to measure the relative concentration of hydrocarbon by observing the length of change of color of the tube. The minimum sensitivity of the tube is 2 ppm of hydrocarbon vapors.

- Metal Oxide Semiconductors (MOS) - The MOS react to hydrocarbon vapors by varying their internal resistance. This

resistance change is then monitored by a circuit and can be calibrated to determine the concentration of hydrocarbon vapors coming into contact with the MOS device. A similar device to the MOS is the adsorption sensor.

There are a number of methods to use this type of device or sensor for monitoring hydrocarbon vapor. The first method is to place a sensor in the monitoring well or probe and connect to a controller. The other method is to draw air samples from the well or probe and pump it through plastic sampling tubes to the sensor mounted in a fixed control box for detection of hydrocarbon vapors.

- <u>Portable Analyzers</u>. There are several types of portable gas analyzers currently available that can be used for monitoring hydrocarbon vapors in wells or probes. Among them are:

  a. Combustible gas indicator also known as gas sniffer or explosimeter uses a heated filament which is part of a resistance measuring circuit. Vapor sample is aspirated into the device and comes in contact with the resistive elements. Any combustible gases present in the sample will be detected by a change in resistance in the circuit due to a change in filament temperature. Detection level of these device can range from 0 to 10,000 ppm of vapor concentration.

  b. Photoionization detectors (PID) is a portable trace gas analyzer with a sensitivity range of 1 ppm to 2,000 ppm. This operates similar to a combustible gas analyzer and can be used to determine the presence and concentration of a wide variety of chemical vapors.

  c. Flame ionization detectors (FID) is a very sensitive instrument designed to measure trace concentrations of organic materials in air. Like the other portable devices, vapor sample is aspirated from the well or probe and analyzed by the device. The FID can measure a wide range of concentrations from 1 ppm to 10,000 ppm of hydrocarbon vapors.

- <u>Continuous Vapor Monitoring Devices</u> These devices combined computer technology with vapor sensors used in portable gas analyzers. Sampling tubes are connected from the wells or probes to a fixed control box which contain the gas analyzer and microprocessor. A pump draws air samples from the probes and analyzed through a bulk semiconductor at least three times a day. The sample is compared to a reference point to determine the presence of high hydrocarbon vapor level. A false alarm feature is incorporated to detect the difference

between a one time spill or a continuing leak. An alarm signal will be activated only after high hydrocarbon vapor level is detected in the same sampling point in three successive readings over a 24-hour period. An internal printer provides a written record of the alarm signals as well other information related to its operation.

SELECTION CRITERIA FOR LEAK DETECTION SYSTEM

In selecting the leak detection technique or monitoring system to be used, consideration must be given to several factors. Most importantly, the system must be capable of detecting leaks particularly the small ones before it affects the groundwater and causes environmental damage. Selection criteria to be considered should include:

1. Effectiveness and sensitivity of the system to detect small leaks as early as possible to protect the environmental from any impairment or damage.

2. Cost of the system, both initial and annual cost, verses its effectiveness to minimize the risk to the owner regarding future environmental damage liabilities.

3. Reliability of the system to function effectively as well as its intrinsic safeguards to avoid hazards.

4. Proven technology with a history of adequate field testing and experience.

5. Ease of operation and maintenance over the life of the system which requires limited operator attention.

6. Ability to screeen out false alarms or to confirm a new ongoing leak before an alarm signal avoids disruption and expensive investigation.

7. Ability to store monitoring data and record alarm situations and other information relevant to its operation and monitoring with audible and/or visual signals to alert the operator in cases of alarm situations.

8. Adequate security to prevent tampering and vandalizing the system as well as safeguarding the information.

9. Continuous and automatic monitoring with audible and/or visual signals to alert the operator in cases of alarm situations.

10. Minimum disruption to the operation of the facility which means no loss of business during monitoring or testing periods.

11. Ability to compensate or account for the sources of error associated with leak detection, inventory reconciliation and tank testing.

12. Applicability to existing underground tanks with minimum installation problems.

13. Subsurface conditions within the tank area and the potential risk of environmental damage.

14. Condition of the tank and underground environment and the risk of tank failure.

Each of these criteria should be carefully evaluated in selecting the appropriate monitoring system. Often no one single leak detection system can satisfactorily address all the criteria of most concern and guarantee maximum protection of groundwater. A combination of monitoring techniques may be necessary to (1) increase system reliability and redundancy to detect leaks and (2) minimize the risk of leak and potential environmental damage.

MONITORING AND ANALYSIS

SHORT-TERM IN VITRO TOXICITY ASSAYS: THEIR CONTRIBUTION TO HAZARD ASSESSMENT

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INTRODUCTION

Growing public awareness of the potential adverse health effects associated with exposure to both man-made and natural toxicants has resulted in increased research in the area of hazard assessment. However, the rate of production of new chemicals is still far greater than the rate of toxicological evaluation. Presently, only animal toxicity tests and human epidemiological studies are believed reliable for assessing human health risks associated with hazardous substances. These analyses are extremely costly (over $ 600,000 per chemical for animal tests), time consuming and limited in sensitivity[1]. Moreover, most human health risks are associated with exposures to chemical mixtures of environmental contaminants. The generation of potentially hazardous waste exceeds 38 million tons each year and there are tens of thousands of chemical dumpsites in this country alone[2]. Long-term toxicity testing or epidemiological studies cannot be used to make proper hazard assessments within a reasonable time frame. As technology advances, the need for more rapid, economical and reliable methodology to evaluate environmental contamination is critical.

In the last fifteen years, short-term *in vitro* assays for detecting chemical mutagens have been developed from the basic knowledge of biochemistry, genetics and molecular biology. The number of different short-term mutagenicity assays is overwhelming yet only a small percentage have been well-characterized[3]. A critical evaluation of the research direction is needed at this time to insure the proper development of these assays for future use. This paper will address the contribution and shortcomings of some *in vitro* short-term tests as they exist today and attempt to predict their value for future hazard assessment.

THE NATURE OF THE BEAST

What is a hazard?

Something that is hazardous is simply something that may cause harm, or has the potential to cause an adverse effect. A hazardous substance may retain the properties of ignitability, corrosivity, reactivity and/or toxicity. To say that all hazards are human toxicants is inaccurate . For example, the strong odors emanating from a meat packing plant may cause psychological harm to those residents of a neighboring community, but the "fumes" are no more toxic than those resulting from your backyard compost pile. It is also wrong to assume that all human toxicants are man-made chemicals and all man-made chemicals are toxic. Mother nature has succeeded in manufacturing many chemical hazards without the aid of technology.

For the purpose of this manuscript, the term hazardous waste refers to those substances either emitted into the environment in uncontrolled amounts (eg., fly ash, industrial wastewaters, automobile exhaust) or confined to dumpsites (eg., storage drums, acid pits). In addition, the term toxicity is defined herein as the ability of a substance to cause genetic damage.

The Problem

Simply stated, the problem that Toxicologists face concerning hazard assessment is how much is too much and too much of what? In other words, what substances are potentially hazardous and what levels should be of concern. A system must be developed to analyze the situation and assess the health risks associated with these substances. This system may be termed the "priority system". Three categories can be defined within this system: 1) hazards with a high risk potential; 2) hazards with a low risk potential; or 3) hazards with insignificant risk potential. Such a system has been proposed for assessing industrial health risks[4]. This system relies on information that will provide an assessment of potency. Those hazardous materials exhibiting a high potency in certain test systems should be considered with high risk potential. Hazards categorized in the high risk group would be given priority over those in the low and insignificant groups.

The Possible Solution

Evaluations as to the relative risks associated with environmental contaminants will aid in deciding the necessary

actions needed to reduce the hazardous potential. In addition, such evaluations can aid in monitoring sites where the potential for contamination is projected but not yet factual. Therefore, the need is for a rapid, economical and accurate analysis for complex chemical mixtures, as would be expected in environmental samples.

SHORT-TERM IN VITRO TOXICITY ASSAYS

There are over one hundred *in vitro* methods for testing toxicity described in the literature[3]. This paper will only discuss assays designed to measure mutagenic activity of chemicals. However, assays to assess ecological toxicity were in use long before the development of the first genetic toxicity assays. The justification of mutagenicity assays is based on the observation that most carcinogens are mutagens. It is also believed that mutations lead to teratogenesis (genesis of birth defects). Therefore the probability is high that if a chemical induces mutations in one or more genetic toxicity test, it may cause irreversible genetic damage .

Predictive Value

The indices of *sensitivity* and *specificity* are calculated to assess the validity of short-term toxicity assays[5]. Sensitivity is defined as the ability of a test to exhibit a positive response in the presence of a carcinogen. Sensitivity is estimated by the proportion of carcinogens yielding a positive response in the assay. Specificity is the ability of a test to properly distinguish between carcinogens and non-carcinogens, and is estimated by the proportion of carcinogens yielding negative results in the assay.

The purpose of short-term assays is to predict whether a substance is carcinogenic or not. Therefore the *predictive value* of a test is ultimately more important than the sensitivity or specificity. The predictive value of a positive test is the probability that a substance testing positive in an assay is actually a carcinogen. Likewise, the probability that a substance exhibiting a negative response is a non-carcinogen is defined as the predictive value of a negative test. Predictive values vary greatly depending on the prevalence of carcinogens in the sampling survey[5]. Therefore, predictive values are not basic properties of the test as are sensitivity and specificity.

To demonstrate the importance of carcinogen prevalence in influencing the estimates of predictive value for short-term assays, assume a test retains the ability to identify correctly 9/10 carcinogens (ie., sensitivity = 90%). The predictive values of both

positive and negative tests can be calculated under two conditions: 1) 1% of all substances tested are carcinogens; and 2) 50% of all substances tested are carcinogens. The results of these calculations for a total of 1000 substances are shown in Tables 1A and B, respectively. While the predictive value of a negative test result remains high (0.98 and 0.90), the predictive value of a positive test varies substantially (0.08 and 0.90).

These theoretical calculations can be compared to what is actually observed (Table 2). When 120 organic chemicals were tested in a bacterial mutagenicity assay (58 animal carcinogens and 62 non-carcinogens), the sensitivity and specificity were estimated at 0.91 and 0.94, respectively[6]. The predictive values for both negative and positive test results were comparable to those calculated in Table 1B. The prevalence of carcinogens in both the observed and expected cases was approximately 50%. Therefore, in theory, if 50% of all chemicals tested in this short-term assay were carcinogens then the overall predictive value of the test would be approximately 90%. On the other hand, if only 1% of all substances were carcinogens (which is probably a more accurate assessment) then the predictive value of a positive test would be less than 10%. In other words, 90% of all positive results may be "false" positives.

A second study indicates that the predictive value for positive test results, when testing only non-carcinogens, is actually significantly better than what is expected[7]. In a test of 70 non-carcinogens, 59% scored a positive result in at least one of four _in vitro_ assays. Therefore the predictive value of the positive test using these chemicals is approximately 40%. Nevertheless, if the predictive value of a short-term assay were in the range of 0.1-0.4 for a survey of substances that retain a low prevalence of carcinogens (1%), it is clear that agents identified as mutagenic _in vitro_ cannot be assumed to be animal carcinogens.

Other Considerations

It should be noted that most carcinogens have been classified as such based on the ability of substances to induce tumors in whole animals. Long-term cancer studies also exhibit inherent sensitivity and specificity further adding to the uncertainty of short-term assays. In other words, the results of short-term _in vitro_ assays rely on the accuracy of whole animal studies to properly identify carcinogens. Because animal studies are not able to accurately identify human carcinogens, without exceptions, this inherent error will add to the overall lower apparent predictive value of _in vitro_ tests. However, the use of animal models to assess potential carcinogenicity is necessitated by the lack of direct experimental evidence implicating chemicals as human carcinogens.

Table 1A

	MUTAGEN		
CARCINOGEN	+	-	PREDICTIVE VALUE
YES	9	99	+ 9/108 = 0.08
NO	1	891	- 891/892 = 0.99

SENSITIVITY = 0.90
SPECIFICITY = 0.90

Table 1B

	MUTAGEN		
CARCINOGEN	+	-	PREDICTIVE VALUE
YES	450	50	+ 450/500 = 0.90
NO	50	450	- 450/500 = 0.90

SENSITIVITY = 0.90
SPECIFICITY = 0.90

Table 1. Predictive Values of a Short-Term Test of 1000 Chemicals. A) 1% are confirmed carcinogens; B) 50% are confirmed carcinogens.

Several other factors may contribute to the low apparent predictivity of short-term assays:

1) Short-term assays may be more sensitive to carcinogens than whole animal studies. Therefore, a substance that is only weakly carcinogenic, and incorrectly determined to be a non-carcinogen *in vivo* , may be positive *in vitro*.

	MUTAGEN		
CARCINOGEN	+	-	PREDICTIVE VALUE
YES	53	5	+ 53/58 = 0.91
NO	4	58	- 58/62 = 0.94

SENSITIVITY = 0.91
SPECIFICITY = 0.92

Table 2. Predictive Value of a Short-Term Test of 120 Chemicals (48% confirmed carcinogens)[7].

2) Because short-term assays are based on a simplified system as compared to whole animals, processes that may inactivate or protect against potential carcinogens, are necessarily lacking *in vitro*.

3) Some substances may possess an inherent genotoxic property, resulting in a positive *in vitro* response, that is not a significant contribution to carcinogenicity .

4) The tests are performed using presumably pure compounds. However, the possibility of the presence of contaminating mutagens cannot be dismissed.

Individual Compounds Versus Complex Mixtures

Of major concern is that while most studies devoted to validating short-term assays rely on the testing of pure, individual compounds, humans are normally exposed to mixtures of impure substances. The complexity of chemical mixtures could greatly affect results obtained from short-term assays. Surprisingly few studies have reported the concomitant testing of environmental complex mixture extracts in both *in vitro* short-term assays and *in vivo* . The lack of information regarding the correlation of *in vitro* results with whole animal studies makes the assessment of human health risks, to environmental contaminants, difficult.

Chemical constituents and subsequent interactions vary from source to source. There are no true "generic" environmental samples. In order to understand the complexity of these samples it is important to define some concepts of carcinogen action.

Concepts of Carcinogenesis

Although the mechanism of chemical carcinogenicity is unknown, it is widely believed that tumor formation is initiated by DNA damage. A chemical that initiates the necessary DNA damage has been termed an ultimate carcinogen. An ultimate carcinogen can be direct acting. However, most chemicals must be metabolically activated to exhibit reactivity. A proximate or pro-carcinogen is regarded as the parent compound or metabolic precursor that is incapable of initiating DNA damage. Some chemicals can increase the metabolism of proximate carcinogens and are called inducers. Chemicals that promote the transformation of a cell but do not initiate DNA damage are called promoters. A complete carcinogen exhibits both initiating and promoting activities. In addition, there are non-carcinogenic chemicals that enhance the activity of a carcinogen when simultaneously present (co-carcinogens),and anticarcinogens that reduce the activity of a carcinogen. A chemical can exhibit any combination of the activities listed above.

Chemical interactions are complex and often difficult to predict. The concepts of synergism and antagonism are frequently used when describing the mechanism of action of complex mixtures. When chemicals interact to increase the response they are acting in synergism. Antagonism describes chemical interactions that decrease the end response.

There are also important relationships between a mixture of chemicals and the organism receiving the dose. Many factors can alter the activity of chemical carcinogens. The more physiologically advanced an organism is, the more factors can be involved. For example, the carcinogenic activity of chemicals in mammals may be influenced by: the species and strain; the sex and maturity of the animal; cell proliferation and target tissue; hormonal and immunological status; the dose and frequency of exposure; and the presence of exogenous or endogenous modifying factors. All short-term in vitro models are deficient in one area; they do not provide an accurate system in which to assess the fate of chemical(s)as expected in humans. Short-term assays are only models and subject to differing interpretations.

Other important aspects of environmental complex mixtures that are often overlooked include methods of sample collection, transport, storage, and most importantly sample preparation. Most environmental samples cannot be added directly to the short-term

test either because of dilution factors or general toxicity. There are no standard procedures for handling environmental samples and frankly there have been few attempts to coordinate these efforts.

DEPLOYMENT OF THE IN VITRO TOXICITY ASSAY

Battery of Tests

Each *in vitro* toxicity test has its own deficiencies. To increase the usefulness of these assay systems it is generally believed that a substance should be tested in a group of complimentary tests. This battery of tests would enable a more complete assessment of the carcinogenic potential based on several assays that measure different endpoints.

Many different combinations of assays have been suggested in the literature, to satisfy the requirements of a battery of tests. Four different test types are represented in this summary, but many others exist. Because of space limitations, details and problems associated with individual assays will not be discussed.

Bacterial Mutagenesis

No assay has been used more than the *Salmonella* His-/His+ assay to assess the carcinogenic potential of chemicals. The "Ames" test measures the reverse mutation of histidine-dependent mutants to histidine-independent. The tester strains contain, in the histidine operon, either DNA base-pair substitutions or frameshift mutations. Therefore these bacteria cannot produce histidine which is essential for their growth. A chemical mutagen can cause a further mutation in this operon, "reversing" the original lesion, allowing for the normal synthesis of histidine and growth of these bacteria. The major deficiency of the Ames assay is the lack of metabolic activity exhibited by these bacteria. Direct acting mutagens can cause a reversion without further activation. However, as mentioned previously, most chemicals must be activated. Activation occurs by a series of chemical oxidations catalyzed by cytochrome P-450-dependent monooxygenases located in most mammalian tissues. These enzymes are found in high levels in liver. Therefore, rat liver fractions can be prepared and added to the medium and co-incubated with the bacteria. This system has proved useful in activating many classes of mutagens.

Preparations of environmental samples have been tested in the Ames test, including: air particulates; automobile exhaust; wastewater extracts; soil extracts; groundwater extract, to name

only a few examples. In most cases concomitant testing in vivo is not performed although positive responses are frequently observed.

Mammalian Cell Mutagenesis

Unlike the Salmonella histidine reversion assay, the majority of mammalian mutagenesis assays measure the forward mutation at a specific genetic locus. In other words, a mutation induced by a chemical will change some activity or phenotype rather than restore it. The most widely used systems measure the appearance of drug-resistant mutants resulting from the forward mutation at one of several important loci. The majority of these tests utilize established cell lines because of their high plating efficiencies, short generation time (<24 hours) and stable karyoptype.

As with the Ames test, most cell lines currently available for mutagenesis studies are incapable of metabolically activating pro-carcinogens. Therefore, these activities must be added either as a fraction of liver homogenates or as co-incubation with nondividing cells possessing the necessary enzymes.

This system has been used less extensively than the Ames assay to assess the carcinogenic potential of individual chemicals. Analyses of air particulates, diesel exhaust extracts, coke-oven emissions and cigarette smoke condensates, to name only a few, have been published using these assays.

Transformation of Mammalian Cells

The use of mammalian cell culture transformation systems is an important aspect of short-term testing for potential carcinogens, since such systems represent most closely the neoplastic transformation in vivo . The endpoint scored most frequently is a morphological transformation usually characterized by a loss of growth inhibition and a subsequent "piling up" of cells.

A major advantage of this system over the mutagenesis assays described above is that many of these culture systems retain the capacity to metabolize and activate pro-carcinogens. However, in some cases co-incubation with nondividing metabolically active cells or the addition of liver fractions is still necessary. In vitro transformation systems can detect a wide range of carcinogens and compliment other methods in that they detect certain carcinogen classes that are negative in most other short-term tests. These assays also require a certain degree of skill and experience in contrast to the mutagenicity.

Although the importance of cell transformation tests cannot be overemphasized, the use of these systems is considerably less than the popular mutagenicity assays. Nevertheless, they have been used to test environmental contaminants. Most notably, extracts of coke-oven emissions, roofing tar, cigarette smoke condensates and diesel emissions have been tested using this model system. In most cases, the results of tests using multiple short-term assays to screen chemical carcinogens yield qualitatively similar results.

Mammalian Cytogenetic Tests

A substantial proportion of carcinogenic agents interact with cellular DNA and are potent inducers of chromosomal damage. In general, DNA damage can be detected cytologically. In multi-test screening of agents for mutagenicity, there has been general agreement on the inclusion of one or more cytogenetic assays in the test battery. Many types of genetic damage can be detected depending on the cell systems used, the stage of cell division studied and the staining methods. Chromosomal aberrations, chromatid aberrations, induction of micronuclei and sister-chromatid exchanges are among the most frequently scored cytogenetic changes.

Cytogenetic damage can be assayed in a variety of cellular systems. Many mammalian cell culture systems, including those used to measure transformations and mutagenesis, are good systems to screen cytogenetic damage. Frequently, cytogenetic screening can be performed simultaneously in cells being used for measuring other endpoints. Another advantage of cytogenetic screening is that it is presently the only method available to detect *in vivo* human genetic changes. Most notably, human lymphocytes have been used to monitor exposures to environmental contaminants.

The major disadvantage of cytogenetic screening for chemical carcinogens is the lack of knowledge concerning the relationship between cytogenetic changes and cellular transformation. However, the use of cytogenetic analyses is warranted because of the superior ability to detect low levels of mutagens and the versatility of these tests. Extracts of coal combustion and air particulates are among the few environmental samples tested using these endpoints.

CONCLUSIONS

The use of short-term *in vitro* toxicity testing to predict potential hazards associated with environmental contamination has demonstrated considerable promise. However, there are still some major deficiencies and problems to be sorted out before these assays can stand on their own. Hazard assessment involves both

qualitative and quantitative measurements. Qualitative evaluations determine the probability that a sample is hazardous using relevant in vitro, in vivo and epidemiological data. Short-term assays, for the most part, correlate well with animal studies in properly identifying genetic mutagens and as such are useful indicators for qualitative assessment.

Quantitative evaluations give an estimate of the relative potency of samples in terms of inherent hazards. Short-term assays do not provide a satisfactory means to predict potency. There is a lack of correlation between assay types as well as between short-term assays and in vivo animal studies. Further research is needed to compare directly the results of short-term assays with those of long-term animal studies in identifying hazards in complex environmental samples. The ultimate goal should be to develop short-term assays as useful predictors of relative risks (high, low and insignificant) in order to prioritize human hazards.

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WASTE LEACHATE/SOIL PERMEAMETRY AS A COMPATIBILITY TEST

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INTRODUCTION

The notion of compatibility between leachate and site soil came into being only recently in the environmental engineering field. In this sense, compatibility represents a measure of the stability of the designed (or simply determined) parameters during the operation of the system. If, for example, an impeding trench is constructed to function at a permeability (K) equal to 10^{-7} $cm \cdot s^{-1}$, the compatibility parameter should indicate the probability that the actual K will deviate from the K value upon exposure to contaminants. The compatibility test, which results in the formulation of a "compatibility parameter," should also provide information on the efficiency of overdesigning to compensate for the expected detrimental effect.

Such a compatibility parameter is lacking at present. Its absence may engender the false assumption that each possible leachate/soil couple is either compatible or incompatible. Definition of a compatibility parameter (similar, for example, to the concept of clay sensitivity in geotechnical engineering) would allow the quantification of compatibility, possibly giving the design engineer information needed to make a system work when the leachate is not perfectly compatible with the soil.

Changes in soil bulk characteristics during and following the permeation of the soil with leachate are most often the consequence of new physico-chemical equilibria established between the clay fraction in the soil and the new fluid (leachate). If the new equilibria are associated with a drastic change in the flocculation/deflocculation or dispersion/aggregation status (such change altering the soil matrix configuration), this could have major effects on bulk characteristics. Among these, permeability may be the property most sensitive to changes in the soil fabric. Leachate/soil compatibility also should be K-range-specific. Thus, a couple can be compatible in a particular range of permeability, for example, around 10^{-6} $cm \cdot s^{-1}$ but not 10^{-7} $cm \cdot s^{-1}$. This is why, ideally, compatibility should be assessed by performing a permeability test simulating field (operational) conditions.

PERMEAMETRY

Studies of solute flow (i.e., migration of salt solutions through soils) performed in the last several decades inspired the technique used today to determine compatibility. Essentially, this is a permeability testing procedure whereby the influent tap water source is changed by the influent solution, the effect of which one wishes to detect. The transient condition is subsequently monitored in terms of both chemical changes in the soil solution and permeability as a function of normalized volume of liquid percolated through the sample.

The test described above has the merit of reproducing field conditions on a small-scale basis, and permitting the monitoring of changes against a unit volume of effluent. The procedure reveals the process of transition from K_1 corresponding to the water to K_2 corresponding to the investigated leachate.

The main deficiencies in this procedure are operational. Some are a consequence of the long period over which monitoring should be done to flush through the sample a "significant" volume of leachate. Such difficulties are only temporary: we have not yet found a way to reconcile the requirements of a minimum sample size, minimum height-to-diameter sample ratio, minimum total flux, and maximum hydraulic gradient when testing a soil that displays a K lower than approximately 10^{-7} $cm \cdot s^{-1}$. For example, if a marginally acceptable soil specimen with a volume equal to 58.5 cm^3 and a height-to-diameter ratio of 0.317 is permeated by a volume corresponding to twice the porosity of the soil ($n = 0.4$) under a hydraulic gradient of 20, and if $K = 3 \cdot 10^{-8}$ $cm \cdot s^{-1}$, the effective testing time will be one month.

This discussion deals specifically with the volume of the effluent required for compatibility-permeametry testing, noted above as a "significant" effluent volume. Some recent trends (CAC, Title 23, Chapter 3, Subchapter 15) appear to indicate that a unique value equal to two pore volumes (PV*) must be flushed through the sample to assess compatibility. We intend to show one way in which the significant volume can be estimated prior to testing. The procedure considers a model which represents a crude simplification of the physical reality. As such, the result will be an approximation and is intended mainly to illustrate the variability of the significant effluent volume or number of pore volumes.

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*1 PV is equal to soil porosity times sample volume, nV, expressed in units of volume (L^3).

SIGNIFICANT EFFLUENT VOLUME

The idea that a flux equal to 2 PV will suffice to assess compatibility seems to have been borrowed from the original work on miscible displacement with salts (Hillel, 1980; Kirkham and Powers, 1971; and Nielsen and Biggar, 1961). In these studies, breakthrough curves (BC) were constructed expressing the change in concentration (as a proportion of the concentration of the replacing solution) versus the number of pore volumes of effluent collected. Figure 1 presents a generalized BC.

A typical BC for an inert constituent would indicate a relative concentration C/C_0 around 0.5 at 1 PV and a C/C_0 of 1 at just less than 2 PV. Although these findings might appear to support the assessment of compatibility at 2 PV, this approach to compatibility assessment has at least two weaknesses.

First, experimental results do not always indicate that at 2 PV C/C_0 is equal to unity, i.e., the original pore fluid is completely replaced by the leachate to be tested. Such is, however, the case with inert solutions--those that do not interact with the soil matrix. For interacting solutes, BC is delayed, approaching $C/C_0 = 1$ at a PV value greater than 2. Thus, to assess the maximum effects induced by fluids that interact with soils and thus change their permeability, a volume of solution greater than 2 PV should be percolated through the sample.

A second reason why a standard 2 PV requirement may not work concerns the fact that BC provides only an average value of C/C_0. It may be argued that for each average C/C_0 recorded at a particular leaching stage, there is a particular distribution of C/C_0 values corresponding to pores of different sizes: the larger the pore, the higher the C/C_0. This situation is illustrated hypothetically on Figure 2.

For the particular distribution presented in the figure, while the overall C/C_0 may be close to unity at stage 7, the C/C_0 corresponding to pores of 0.1 μm is only 0.6. Since small pores are associated with finer soil particles, it is probable that--despite the large overall C/C_0--the fine clay (the behavior of which may control the behavior of the whole soil) has not yet been "treated" at stage 7. It would thus be premature at this stage of the leaching event to attempt to infer system compatibility.

ESTIMATION OF EFFLUENT VOLUME REQUIRED TO ASSESS COMPATIBILITY

Knowledge of the minimally significant total flux required to assess compatibility, determined before performing the permeametry test, is certainly useful. Such knowledge should be available as a calculated parameter; it should be closely correlated with the true

pore volume parameter. Formulation of such a parameter--which we will call an estimator of number of pore volumes, N_{PV} must consider that the significant flux volume is a function of both soil properties and solute characteristics. The basic assumptions behind the formulation of N_{PV}, qualitatively stated, are as follows:

1. The more "different" the leachate compared to the equilibrium soil solution, the greater the likelihood that changes will be induced in the soil.

2. The lower the soil cation exchange capacity (CEC_s) and the higher the concentration of the critical constituent in the leachate C_0 (the constituent with the highest potential for inducing changes), the faster these changes will occur, and thus the smaller the PV value required to detect the existing incompatibility.

3. All other factors being equal, the lower the CEC_s, the lower the magnitude of incompatibility (if incompatibility exists).

The N_{PV} parameter is specifically formulated for the case in which the critical constituent is represented in the leachate by a cation. Thus it is necessary to know the cation exchange capacity and the proportion of the capacity that was originally saturated with the considered cation.

Another soil parameter of significance is porosity. A lower porosity (i.e., a lower moisture content at saturation) requires a greater volume of percolated liquid to produce a certain effect on a unit mass of soil.

Input solution parameters are the concentration of the critical constituent in the leachate and in the original (uncontaminated) soil solution, and the mass-equivalent value of the constituent.

The estimator of PV is defined as follows:

$$N_{PV} = \frac{CEC_s(1-P)}{SPV} \times \frac{M_{equiv}}{C_0(\frac{1}{1-P'})}$$

where

CEC_s is the cation exchange capacity of the soil (m.equiv$\cdot g^{-1}$)

SPV is the specific pore volume ($L \cdot g^{-1}$)

M_{equiv} is the mass equivalent of the constituent ($\bar{g} \cdot$m.equiv^{-1})

C_0 is the concentration of the constituent ($\bar{g} \cdot L^{-1}$)

P is the proportion of CEC_s saturated with the considered cation prior to leachate exposure

P' is the proportion of C_0 found in solution prior to leachate exposure.

The first term of the right-hand side of the expression for N_{PV} is the "soil term," while the second is the "solution term." The SPV is the PV value normalized per unit mass of soil. If $P > 0.5$, N_{PV} will be relatively small, but the effect on permeability may not be significant because the cation was abundantly present in the soil matrix prior to exposure. If $P' > 0.5$, N_{PV} will be relatively small, but the effect on permeability may not be significant because the cation was abundantly present in the soil solution prior to exposure. N_{PV} is a unitless parameter.

Although N_{PV} does not lead directly to the value of total flux required to assess incompatibility, it should be strongly related to this value. Therefore, it will be useful to perform a simple numerical analysis to assess the range of variability of N_{PV} when reasonable values are assigned to the parameters in the expression for N_{PV}. If the estimator N_{PV} is found to be relatively insensitive to variation of parameters, then the use of a unique flux may be appropriate in assessing incompatibility. Whether PV is equal to 2 or 5 or any other number remains to be determined. On the other hand, if a high variation of N_{PV} is observed when the parameters are varied reasonably, then a unique value of pore volume (irrespective of soil and solution characteristics) may not be appropriate in assessing incompatibility. Tables 1 and 2 present the values of different parameters for which the "soil term" and the "solution term" of N_{PV} were calculated. P and P' were assumed to be equal to zero in these calculations.

Table 1. Range of cation exchange capacity of clay fraction, CEC_c (m.equiv$\cdot g^{-1}$), percent clay, and specific pore volume ($L\cdot g^{-1}$) for which "soil terms" were calculated

Soil Characteristics	Range Considered
CEC_c (m.equiv$\cdot g^{-1}$)	0.2 to 0.8
Percent Clay	15 to 35
Soil Bulk Density (pcf)	95 to 127
and corresponding SPV assuming specific density 2.68 $g\cdot cm^{-3}$	$2.834\cdot10^{-4}$ to $1.180\cdot10^{-4}$

Table 2. Range of solution concentration, C ($\bar{g} \cdot L^{-1}$) and mass equivalent ($\bar{g} \cdot$m.equiv^{-1}) for which "solution terms" were calculated

Solution Characteristics	Range Considered
C ($\bar{g} \cdot L^{-1}$)	1.5 to 6.0
M_{equiv} ($\bar{g} \cdot$m.equiv^{-1})	0.035 to 0.085

Figure 3 maps the values of the first ("soil") term in the expression for N_{PV} as a function of the cation exchange capacity of the soil ($CEC_s = CEC_{clay}$ x (percent clay/100)) and its bulk density (pcf). SPV values corresponding to the densities indicated on the ordinate were considered in the calculation of the "soil term."

As can be seen from the figure, even when only a moderate variation of soil parameters is considered, the "soil term" takes values over a range greater than one order of magnitude. While at CEC_s = 0.1 m.equiv$\cdot g^{-1}$ the soil term takes a value around 200 m.equiv$\cdot L^{-1}$, at relatively large values of CEC_s and large densities it has a value around 1500 m.equiv$\cdot L^{-1}$. At low values of CEC_s, this parameter almost completely overshadows the effect of density on the soil term. Strictly from the standpoint of the cation exchange capacity and density, soils vary considerably and thus the soil term is likely to affect to a great extent the volume of the effluent required to assess incompatibility.

Figure 4 maps the values of the second ("solution") term in the expression for N_{PV} at different M_{equiv} ($\bar{g} \cdot$m.equiv^{-1}) and C ($\bar{g} \cdot L^{-1}$). The figure shows that the "solution term" also varies over a relatively broad range. This term is relatively stable in the case of cations of low atomic weight and high valency at relatively high concentrations. However, when the considered cation has a high atomic weight, a low valency, and a concentration within the solution that is moderate but still high enough to promote incompatibility, the solution term becomes quite sensitive.

According to Figures 3 and 4, the product of the soil and solution terms (which is the N_{PV} parameter) can have values between 0.6 and over 100. When 1) the soil has a relatively low cation exchange capacity and (eventually) a low bulk density, and 2) the cation the effect of which is being investigated is at a relatively high concentration and of low atomic weight and high valency, then N_{PV} is smaller than 15. When 1) the soil has a relatively high cation exchange capacity and high bulk density, and 2) the cation the effect of which is being investigated is at a moderate concentration and (eventually) of high atomic weight and low valency, then the N_{PV} is larger than 50.

N_{PV} is not a direct indicator of the exact number of pore volumes of fluid that should be moved through the soil before compatibility can be assessed. However, this parameter should correlate strongly to the true PV value; for this reason, we call it an estimator.

Tentatively, values of N_{PV} lower than approximately 10 may be associated with conditions in which 2 PV should suffice to ascertain compatibility. When the calculated N_{PV} is larger than 30, it is probable that an inordinately high number of pore volumes will have to be moved through the soil to assess compatibility. This is true particularly in view of the fact that a high N_{PV} will normally result from a high proportion of active clay and a high density; both of these characteristics promote a low hydraulic conductivity. In such a case (when N_{PV} is large), soil/leachate compatibility should be assessed using a different procedure. Such a method may be the subject of a future presentation.

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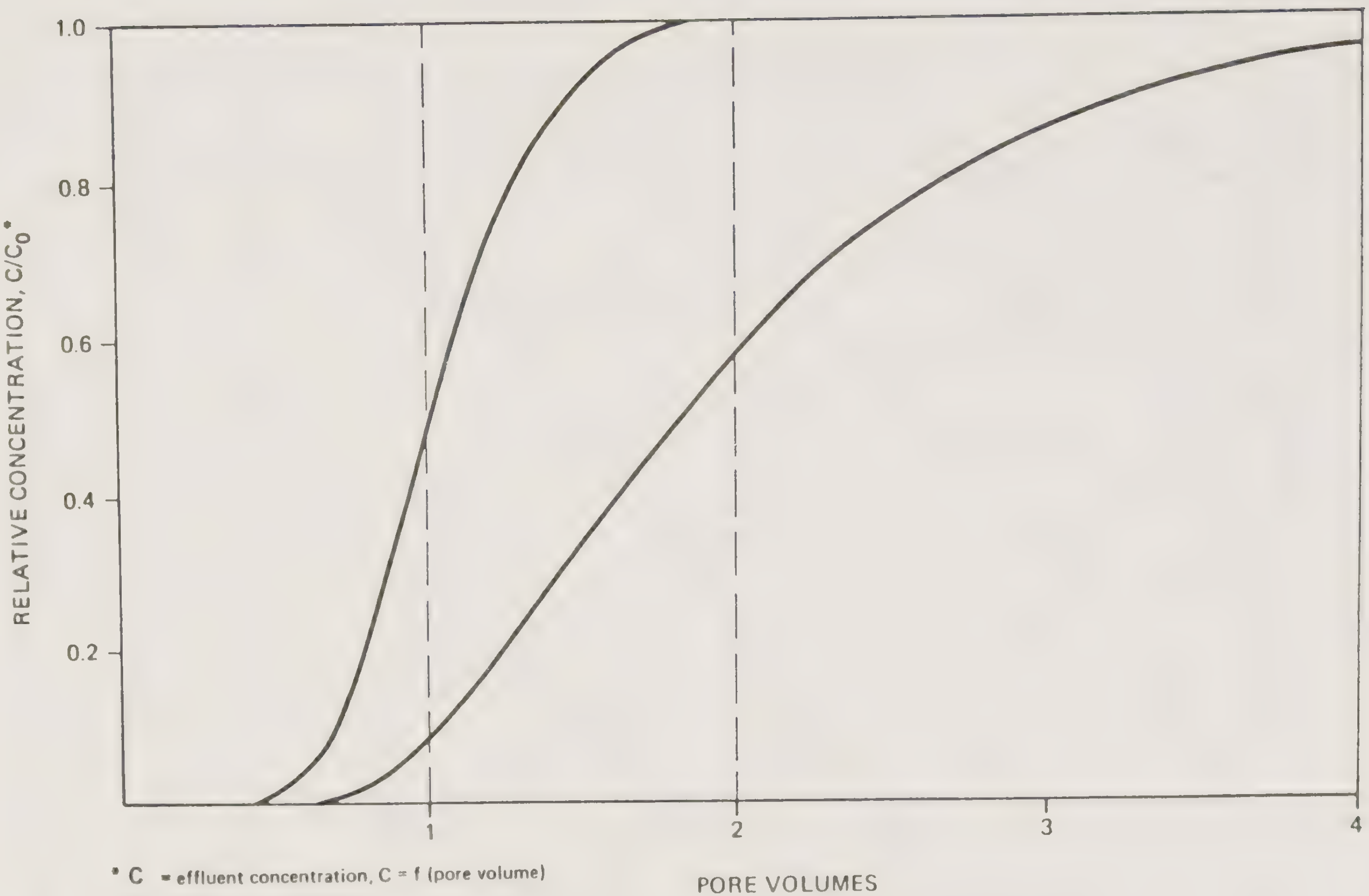
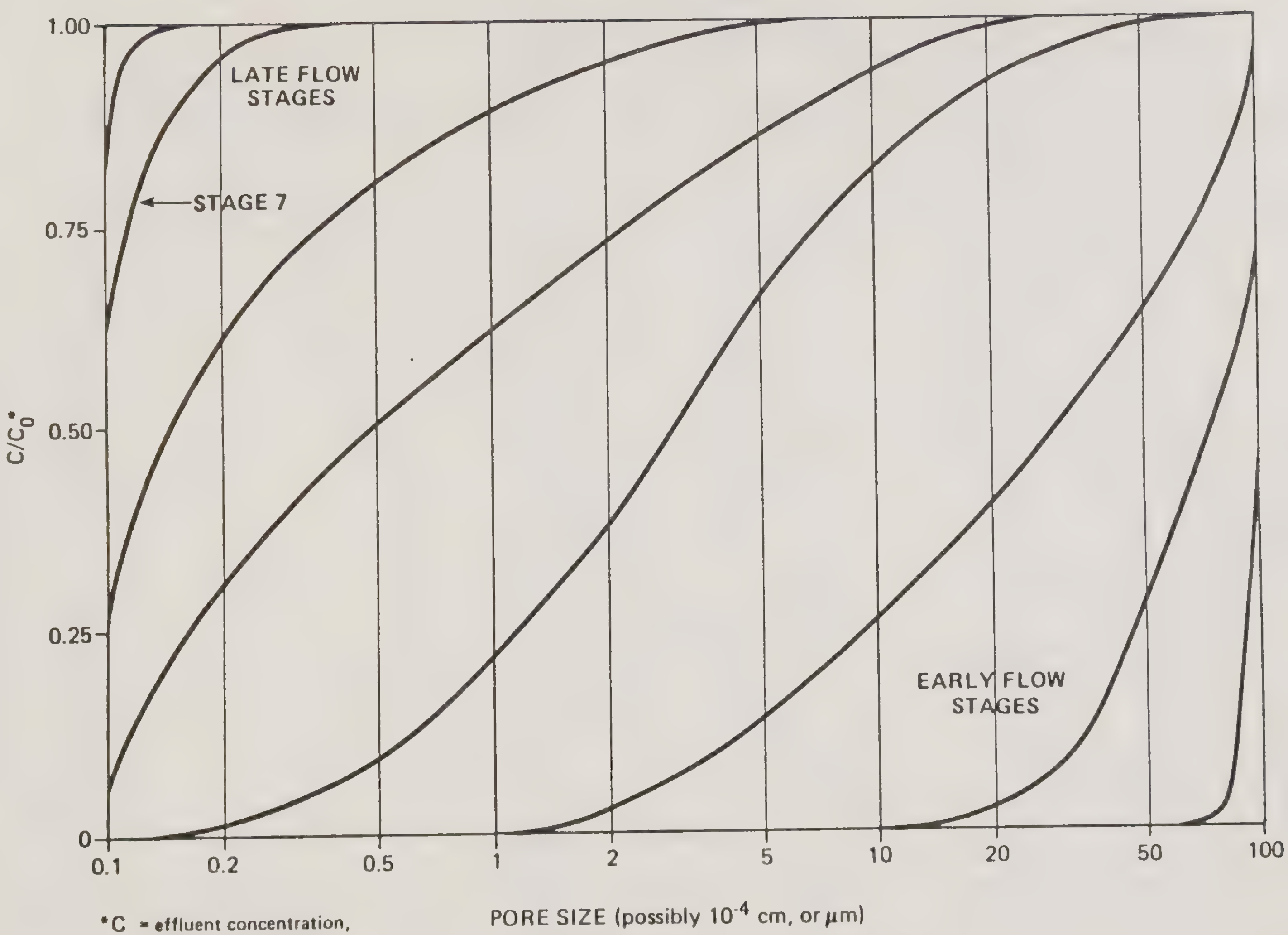


* C = effluent concentration, C = f (pore volume)
C_0 = influent concentration

Figure 1. Hypothetical Breakthrough Curves



*C = effluent concentration, C = f (pore volume)

C_0 = influent concentration

Figure 2. Hypothetical relative concentration values for pores of different sizes at different stages of a solute flow event.

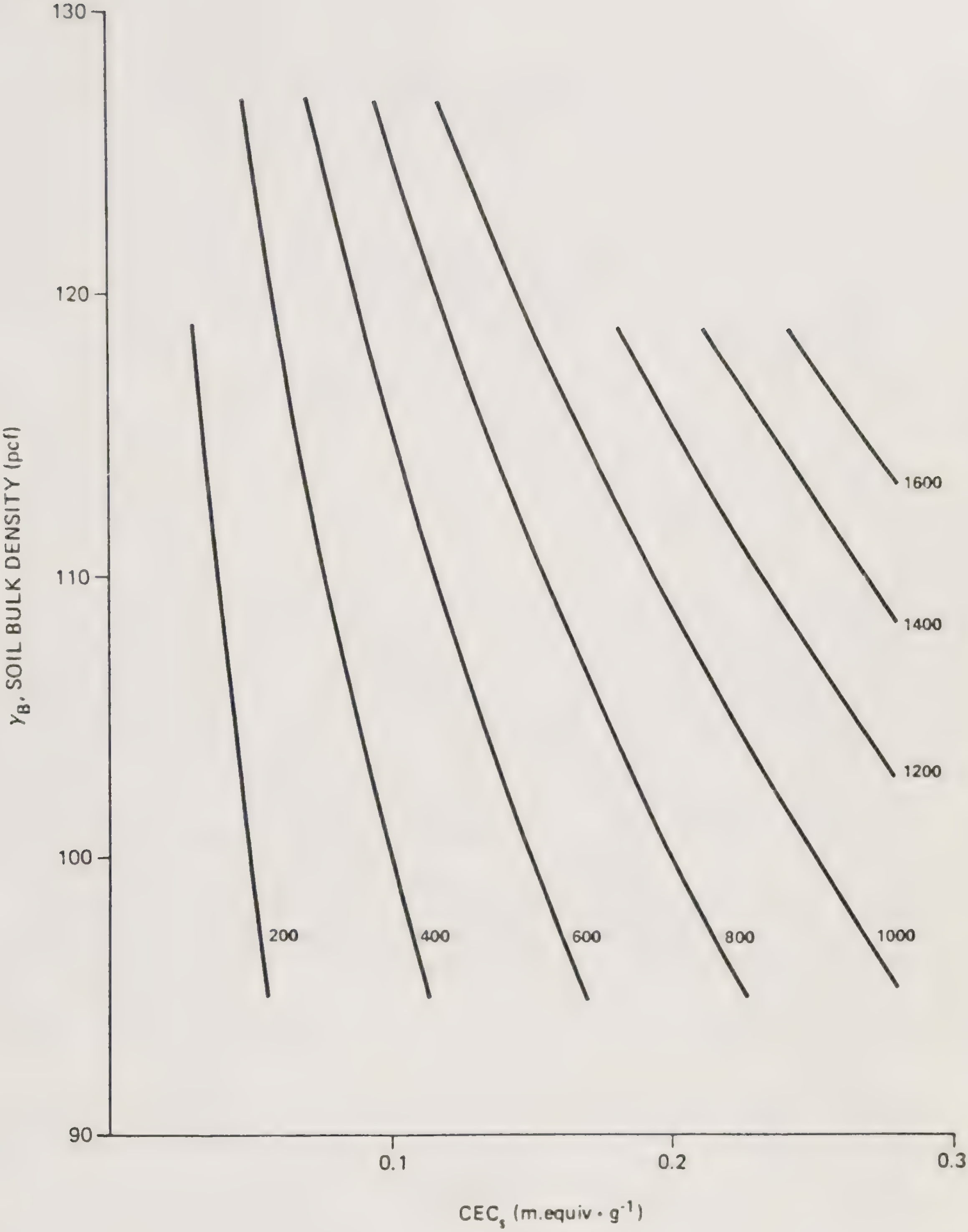


Figure 3. The value of the "soil term" (m.equiv · L^{-1}) in the expression N_{PV} = (soil term) x (solution term).

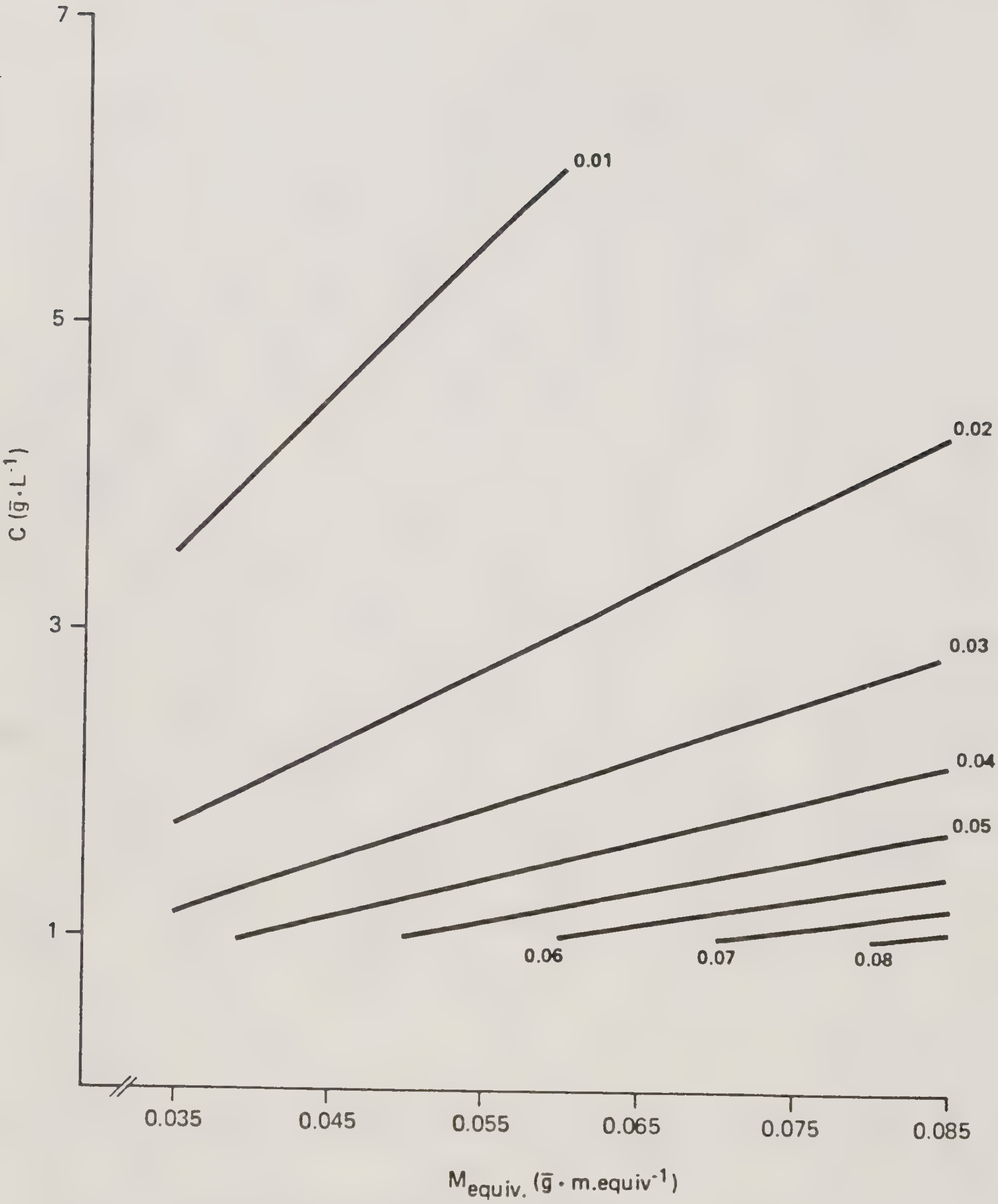


Figure 4. The value of the "solution term" ($L \cdot m.equiv^{-1}$) in the expression N_{PV} = (soil term) x (solution term).

IDENTIFICATION OF TARGET COMPOUNDS IN HAZARDOUS WASTES BY MASS SELECTIVE DETECTOR

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ABSTRACT

With the expanding requirements of state and federal programs for regulating hazardous wastes, the need for rapid and accurate characterization of potentially hazardous materials has become increasingly important. Recently, demands for environmental sample analysis in the laboratory at the California State Department of Health Services have dramatically increased. The complexity of the matrices of hazardous waste samples often exceeds the selectivity of standard analytical techniques and requires verification data from gas chromatography/mass spectrometry. A selective, sensitive and cost-effective analytical technique has been developed for this task.

A mass selective detector (MSD) is directly coupled to a high resolution GC capillary column. The mass spectrum generated by GC/MSD provides evidence for positive compound identification. Selective ion monitoring on characteristic ions yields enhanced detection limits and improved signal to noise ratio. Analysis based on specific ions present within a narrow retention time window provides qualitative information and accurate, interference-free quantitation.

This study describes the methodology developed for the routine monitoring of organic priority pollutants. The application of GC/MSD for detection at low levels will be discussed. Results of a comparative study for the analysis of priority pollutants between Finnigan 4500 and Hewlett Packard Mass Selective Detector will be reported. Specific examples analyzed by the Hazardous Materials Laboratory will be presented.

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INTRODUCTION

Implementation of current environmental legislation such as the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) requires accurate analytical data. The U.S. Environmental Protection Agency (EPA) has developed a series of methodologies and instrumental techniques for monitoring environmental pollutants (1,2,3). The resultant phenomenal growth in demand for analyses presents new challenges and needs for both private and government laboratories. Recently, the California Department of Health Services, Hazardous Materials Laboratory, has established a program for certification of laboratories performing environmental analyses. At present approximately 100 private laboratories are pending certification.

The determination of target compounds at low levels within complex matrices presents a challenge to the environmental analyst. The complexity of sample matrices often exceeds the selectivity of standard analytical techniques which necessitates long extensive clean-up prior to sample analysis. Potential litigation requires rapid and accurate analytical results. The combination of gas chromatography and mass spectrometry (GC/MS) provides one of the most powerful systems available for these analyses. The mass spectrometer is a universal detector which can be made selective to allow preclusion of interferences. Selective Ion Monitoring (SIM), widely used in the biomedical and environmental fields, is a highly sensitive and selective means of detection and quantitation. For samples with a high level of interference, data generated by GC/MS can provide qualitative information as well as quantitative accuracy. However, the application of GC/MS is often limited by its high cost, system maintenance requirements, and the need for trained operators. The introduction of compact mass spectrometric detectors for capillary column gas chromatography has broadened the scope of many analytical laboratories. Two commercial models, Finnigan MAT ion trap detector (ITD) and Hewlett Packard mass selective detector (MSD) are currently available. The application of these two instruments in environmental analyses has been reported (4,5). These instruments have been characterized by the relative simplicity in design, ease of operation, low maintenance and modest cost. Recently, the laboratory certification group at the Hazardous Materials Lab has received requests to certify analyses employing GC/ITD or GC/MSD as alternative techniques for determination of organic priority pollutants.

To support the certification program, the capability of GC/MSD system for the analysis of semivolatile organics was recently evaluated in our laboratory. This paper presents the summary of our study and the application of this system in analysis of low level target compounds in hazardous wastes.

INSTRUMENT COMPARISON

To assess the validity of using the mass selective detector as an alternative analytical tool for hazardous waste analysis, a comparative study of a Finnigan 4500 GC/MS and Hewlett Packard 5890/5970 GC/MSD was undertaken. A series of identical samples were analyzed with each instrument.

An essential question regarding the acceptability of the MSD is whether it could be tuned to generate mass spectra of decafluorotriphenylphosphine (DFTPP) which meet the criteria established by EPA (6). For routine tuning of the MSD, the reference compound, perfluorotributylamine (PFTBA), and an automated program, autotune, are used to set operating parameters. The manufacturer has published a procedure for adjusting the autotune parameters to tune the MSD to meet EPA criteria (7). With slight modification of this procedure, the MSD was easily tuned and routinely produced acceptable mass spectra of DFTPP. Generally, the ion focus voltage was increased from its autotune value to produce a mass spectrum of PFTBA with mass ions 131 and 219 having equal abundance.

As part of the requirements for quality assurance, both instruments were tuned to meet EPA criteria. The tuning was verified daily by injection of DFTPP (50 ng.) through the GC inlet. To evaluate the accuracy and precision of the analysis, a set of EPA quality control (QC) samples containing acid, base, and neutral priority pollutants was extracted and analyzed. Extracts in dichloromethane were prepared in accordance with EPA test method 8270 (2).

Chromatography prior to MSD analysis was performed with a HP 5890 gas chromatograph and a fused silica capillary column (5% phenylmethylsilicone, 25 m x 0.20 mm, 0.33 mm film thickness). The column outlet was connected directly to the ion source of the HP 5970 MSD. The total ion current was scanned over a m/z range of 35 to 450 with a scan time of 1.10 second. Extraction and integration of a characteristic ion within a narrow time window was used for screening, tentative identification, and quantitation. Usually the characteristic ion was the primary ion recommended by EPA (2) and the time window was $\pm$ 2.5% of the expected retention time. The internal standard method was used with D6-phenol as the reference for acids and D8-naphthalene or D10-anthracene for the base/neutrals. Quantitation was based on previously established calibration tables and the integrated areas of the characteristic ions and internal standard. Table 1 is a typical three level calibration table for phenols. A similar table was prepared for 45 base/neutral priority pollutants. In routine operation, the retention times in the calibration table can be updated and response factors recalibrated or averaged, if necessary, whenever a standard is run.

TABLE 1 *** Calibration Table ***

DATA:ACCALJH.Q

Last Update : 15 Jan 86 2:39 pm
Sample Amount : 0.000
MultiLevel Curve Fit : Linear
Reference Peak Window : 5.00 % of Retention Time
Non-Reference Peak Window : 5.00 % of Retention Time
Uncalibrated Peak Response Factor : 0.000 Dilution Factor : 1.000

Ret Time	Pk #	Ch Description		Amt ng/ul	Lvl	[Area]	Pk-Type		Partial Name
7.804	1	Ion	99.0	40.00	1	171173	+IS	1	D6-PHENOL
7.826	2	Ion	94.0	5.000	1	32139		1	PHENOL
				10.00	2	62061			
				25.00	3	151908			
8.114	3	Ion	128.0	5.000	1	20791		1	2-CL-PHENOL
				10.00	2	43381			
				25.00	3	102652			
10.723	4	Ion	139.0	5.000	1	7162		1	2-NO2-PHENOL
				10.00	2	16995			
				25.00	3	46731			
10.831	5	Ion	122.0	5.000	1	14871		1	2,4-ME-PHENOL
				10.00	2	28325			
				25.00	3	75605			
11.274	6	Ion	162.0	5.000	1	15099		1	2,4-CL-PHENOL
				10.00	2	31621			
				25.00	3	79806			
13.087	7	Ion	142.0	25.00	1	73249		1	4CL-3ME-PH
				50.00	2	128408			
				125.0	3	338843			
14.197	8	Ion	196.0	15.00	1	34287		1	2,4,6-CL-PH
				30.00	2	69293			
				75.00	3	174059			
16.333	9	Ion	184.0	15.00	1	7454		1	2,4-NO2-PH
				30.00	2	20448			
				75.00	3	83452			
16.504	10	Ion	65.0	25.00	1	47410		1	4-NO2-PH
				50.00	2	98538			
				125.0	3	297704			
17.771	11	Ion	198.0	25.00	1	30050		1	2ME-4,6NO2-PH
				50.00	2	69263			
				125.0	3	230355			
19.605	12	Ion	266.0	25.00	1	55402		1	PENTA-CL-PH
				50.00	2	103880			
				125.0	3	288367			

The operations of ion extraction, initial screening, integration, quantitation, and report generation can be automated using the run/report software of the MSD and macro programs. Details of the analytical procedures and automation to use the MSD to screen for target compounds in hazardous wastes have been reported (8). Recently the macro program has been modified to obtain a detailed graphic representation of each extracted ion after integration. Thus, the analyst has a visual opportunity to verify that each ion had been integrated properly and that no problem with overlapping "ion-peaks" had occurred. Figure 1 is an example of the graphics for four extracted ions. To assure that the quantitation report is valid, the ion for the internal standard and ions for each target compound should appear in the center of their respective time windows and the integration should be normal.

For the comparison of instrumental performance, aliquots of each sample extract were subjected to analysis in a Finnigan 4500 GC/MS system using a DB-5 fused silica column (30 m x 0.25 mm). Compound identification and quantitation were accomplished by the Incos data system using reverse library search and programs edited for "Target Compound Analysis" (TCA). A mass spectral library and quantitation table used for TCA were created from authentic standards purchased from Supelco, Inc.

Analytical results for the acid fraction are summarized in Table 2. Upon consideration of the limitation of using the scan mode of data acquisition to monitor narrow GC peaks, the results from the two instruments compare favorably. The concentration levels determined by the Finnigan 4500 generally are slightly higher than those from MSD data. The concentration levels found by the two instruments differ by an average percent difference of 14%. An apparent percent recovery based on the EPA QC level was calculated from the concentration level determined by each instrument. The apparent percent recovery reflects both the extraction efficiency and response factor generated by the instrument's software. The average of the apparent percent recovery values for the 4500 is 80% with a standard deviation of 25%. For the MSD the average is 75% with a standard deviation of 24%. The concentration detected for 2,4-dimethylphenol was unexpectedly low for both instruments. If this value is excluded the average apparent percent recovery is 88% with a standard deviation of 13% for the Finnigan 4500 and 81% with a standard deviation of 13% for MSD.

TABLE 3 summarizes the analytical results for the base/neutral fraction of the quality control sample. Again, the concentration levels based on the MSD data are slightly lower than the 4500 levels but generally compare favorably with the 4500 values. The average percent difference in the concentration levels determined by the two instruments is 23%. The average of the apparent percent recovery values is 89% with a standard deviation of 18% for the 4500, and 72% with a standard deviation of 19% for the MSD.

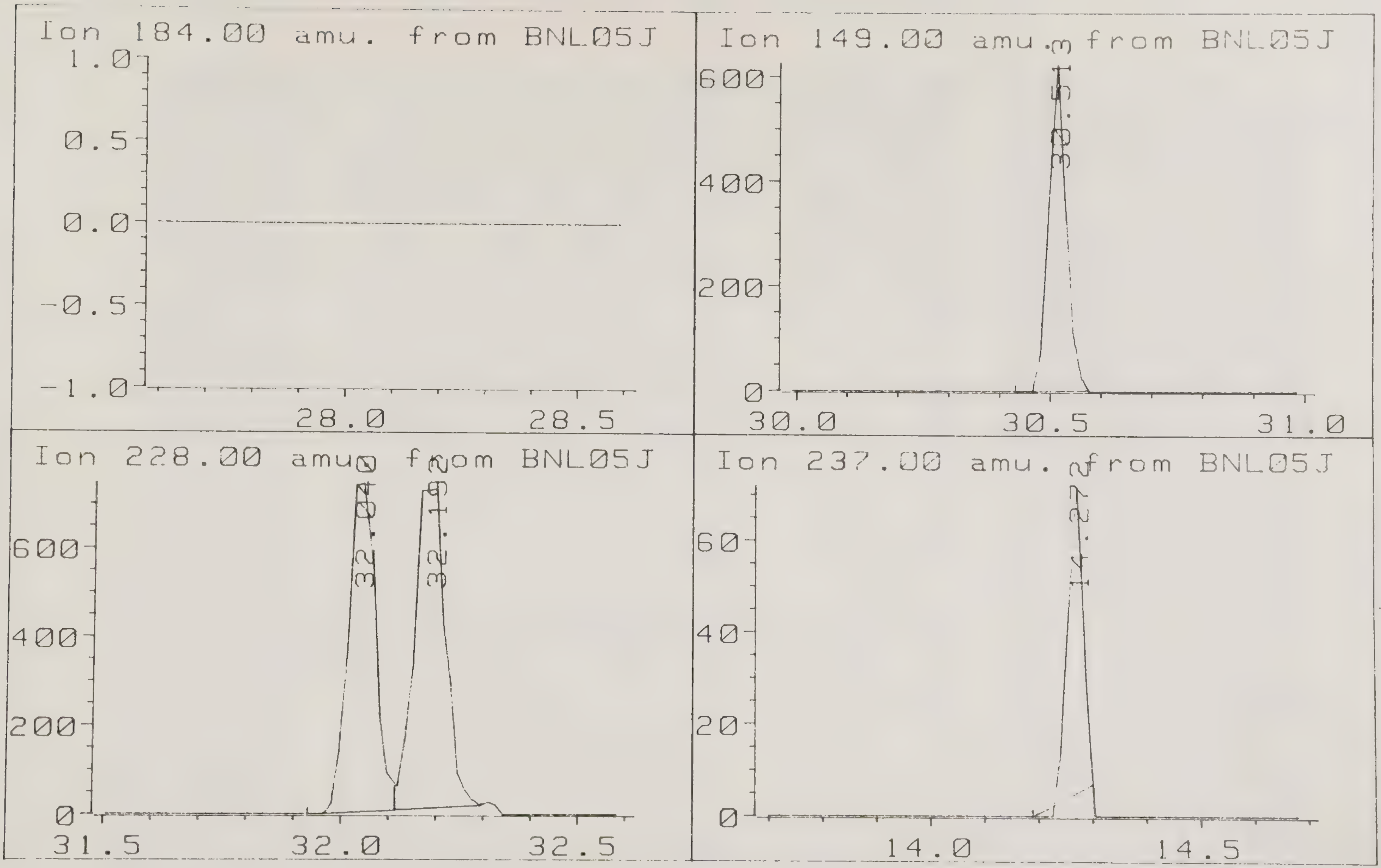


FIGURE 1 CHROMATOGRAMS OF FOUR EXTRACTED IONS

TABLE 2 Acid Fraction of Quality Control Sample

COMPOUND IDENTIFIED	*EPA QC (µg/L)	CONCENTRATION (µg/L) 4500	MSD	% DIFFERENCE	APPARENT % RECOVERY 4500	MSD
Phenol	100	66	59	11	66	59
2-chlorophenol	30	28	23	20	93	77
2-nitrophenol	50	52	40	26	104	80
2,4-dimethylphenol	30	5	5	0	17	17
2,4-dichlorophenol	50	45	41	9	90	82
4-chloro-3-methylphenol	75	67	63	6	89	89
2,4,6-trichlorophenol	25	22	21	5	88	88
4-nitrophenol	50	34	49	36	68	68
2-methyl-4,6-dinitrophenol	250	234	177	28	94	94
pentachlorophenol	75	72	74	3	96	96
Average %				14	**88 (σ = 13)	**81 (σ = 13)

* Concentration in deionized water before extraction.

** Values for 2,4-dimethylphenol were excluded from the average

1. Data presented are the average of duplicate analyses.
2. % recovery of surrogate, 2-fluorophenol spiked at 50 µg/L, was 77% for Finnigan 4500 and 79% for MSD.
3. EPA Water Pollution Quality Control Sample WP 881 Sample 1.
4. Apparent % recovery = (concentration/EPA QC concentration) x 100.

TABLE 3 BASE/NEUTRAL FRACTION OF QUALITY CONTROL SAMPLE

COMPOUND IDENTIFIED	*EPA QC (μg/L)	CONCENTRATION (μg/L)		% DIFFERENCE	APPARENT % RECOVERY	
		4500	MSD		4500	MSD
Bis(2-chloroethyl)ether	>53	185	165	11	73	65
1,3-dichlorobenzene	148	101	91	10	68	61
1,2-dichlorobenzene	250	176	146	18	70	58
N-nitroso-N-propylamine	352	320	206	43	91	59
Isophorone	149	127	88	36	85	59
Bis(2-chloroethoxy)methane	255	216	174	21	85	68
1,2,4-trichlorobenzene	256	199	150	28	78	59
Hexachlorobutadiene	157	95	88	7	61	56
2-chloronaphthalene	251	218	140	43	87	56
2,6-dinitrotoluene	229	254	204	21	110	89
2,4-dinitrotoluene	277	300	247	18	108	90
Diethyl phthalate	254	156	153	2	61	60
Hexachlorobenzene	350	354	270	26	101	77
Phenanthrene	202	194	168	14	96	83
Dibutyl phthalate	252	277	328	16	110	130
Pyrene	298	308	296	4	103	99
Benzo(a)anthracene	315	361	237	41	114	75
Dioctyl phthalate	230	---	137	—	---	60
Benzo(k)fluorothene	246	260	157	49	105	64
Average %					89 (σ = 18)	72 (σ = 19)

* Concentration in deionized water before extraction.
1. Data presented are the average of duplicate analyses.
2. % of surrogate recovery, 1-fluoronaphthalene spiked at 50 μg/L,was 73% from Finnigan 4500 and 70% from MSD.
3. EPA water Pollution Quality Control Sample WP 482 Sample 2.
4. Apparent % recovery = (concentration/EPA QC concentration) x 100.

As part of this study, two environmental samples were also analyzed under the same analytical conditions. Unfortunately, none of the target compounds was detected in either sample. However, the percent recovery of spiked surrogates determined by these two instruments were found to be in the same range for both the environmental and EPA QC samples. Compound identification using library search against NBS mass spectral database for pollutants showed a matching index of over 9000 for MSD.

SELECTIVE ION MONITORING

It is quite common for chromatograms of hazardous waste samples to contain hundreds of peaks. A procedure involving selective ion monitoring has been developed which allows one to screen for priority pollutants in the presence of high background contamination (8). Three characteristic ions for each target compound were monitored in a defined time window. The simultaneous detection of all three ions at the expected retention time is an indication of the presence of the target compound. The area of the primary ion can be used for quantitation based on a calibration table established under the same analytical conditions with SIM. With this technique, target compounds can be rapidly identified from complex matrices without library search. The application and advantages of using SIM acquisition when analyzing hazardous waste will be illustrated in the following examples.

The first is the analysis of a black sludgy sample collected from an aluminum anodizing company in Hayward, California. The sample extract was first screened by GC equipped with a flame ionization detector. About 30 peaks were found. Five were tentatively identified as acenaphthalene, fluorene, fluoranthene, chrysene and bis (2-ethylhexyl)phthalate. For confirmation the sample extract was further analyzed by GC/MSD. The chromatogram acquired from total ion scanning is presented in Fig. 2A. A complete library search of these peaks is a long process and may be limited by inadequate computer memory. With the technique of SIM as described above, a program was set up to screen for 45 basic and neutral target compounds. Fig. 2B is the chromatogram acquired from SIM. In this chromatogram, only the added internal standard, D10-anthracene, and a trace of bis(2-ethylhexyl)phthalate were detected. To demonstrate the validity of this screening program, a mixture containing eight base/neutral standards was spiked into the sample extract at the concentration of 20 μg/ml. Upon analyses of the spiked extract under the same conditions, these compounds were clearly identified in chromatogram 2C. The pattern of the chromatogram shown in Fig. 2A suggested that the major components may be hydrocarbons. These components were identified as straight chain hydrocarbons by the matched extracted ion current profile for masses 43, 57, 71, 85, 99 and 127 as shown in Fig 3.

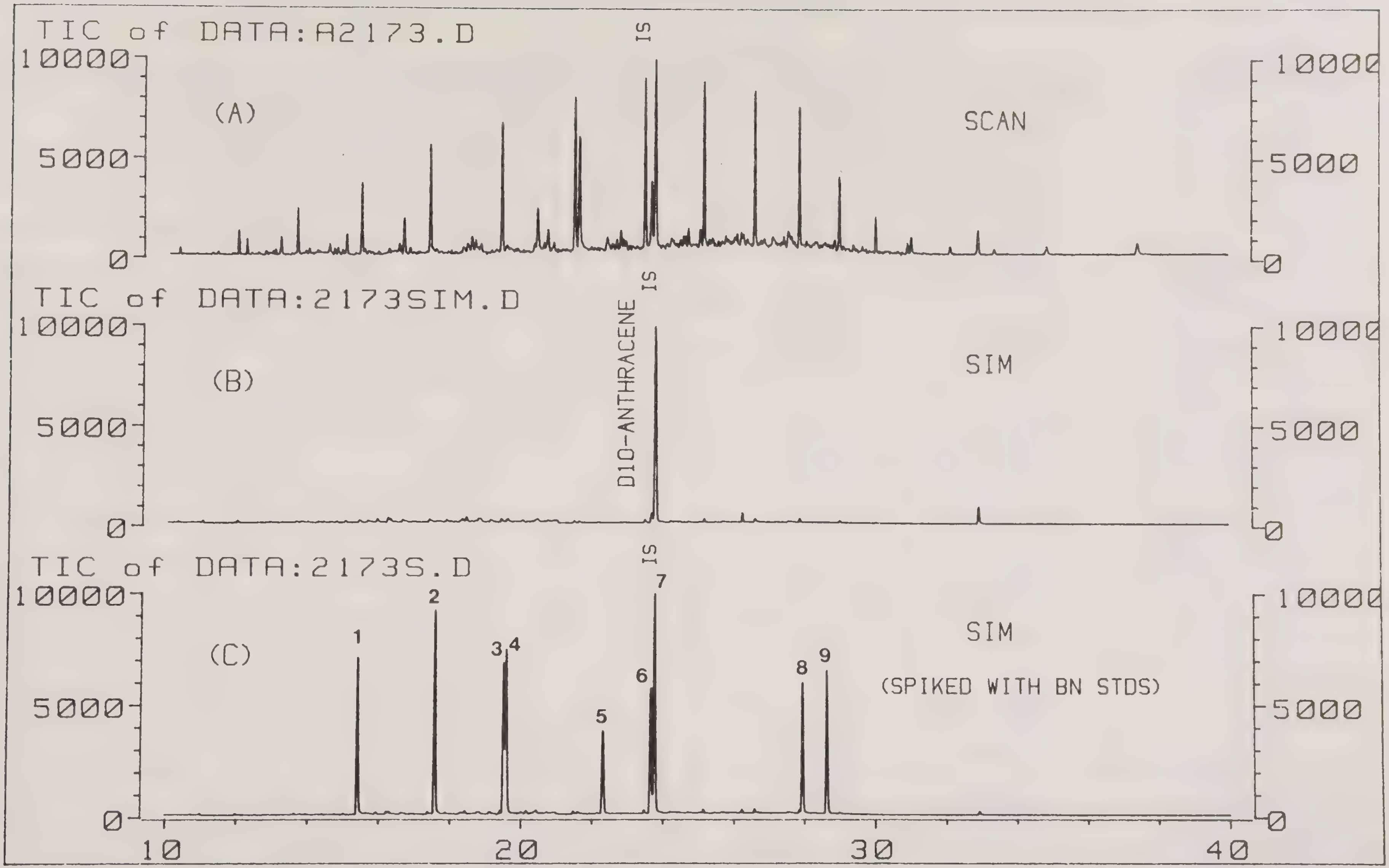


FIGURE 2 GC/MS ANALYSIS OF A SLUDGY SAMPLE

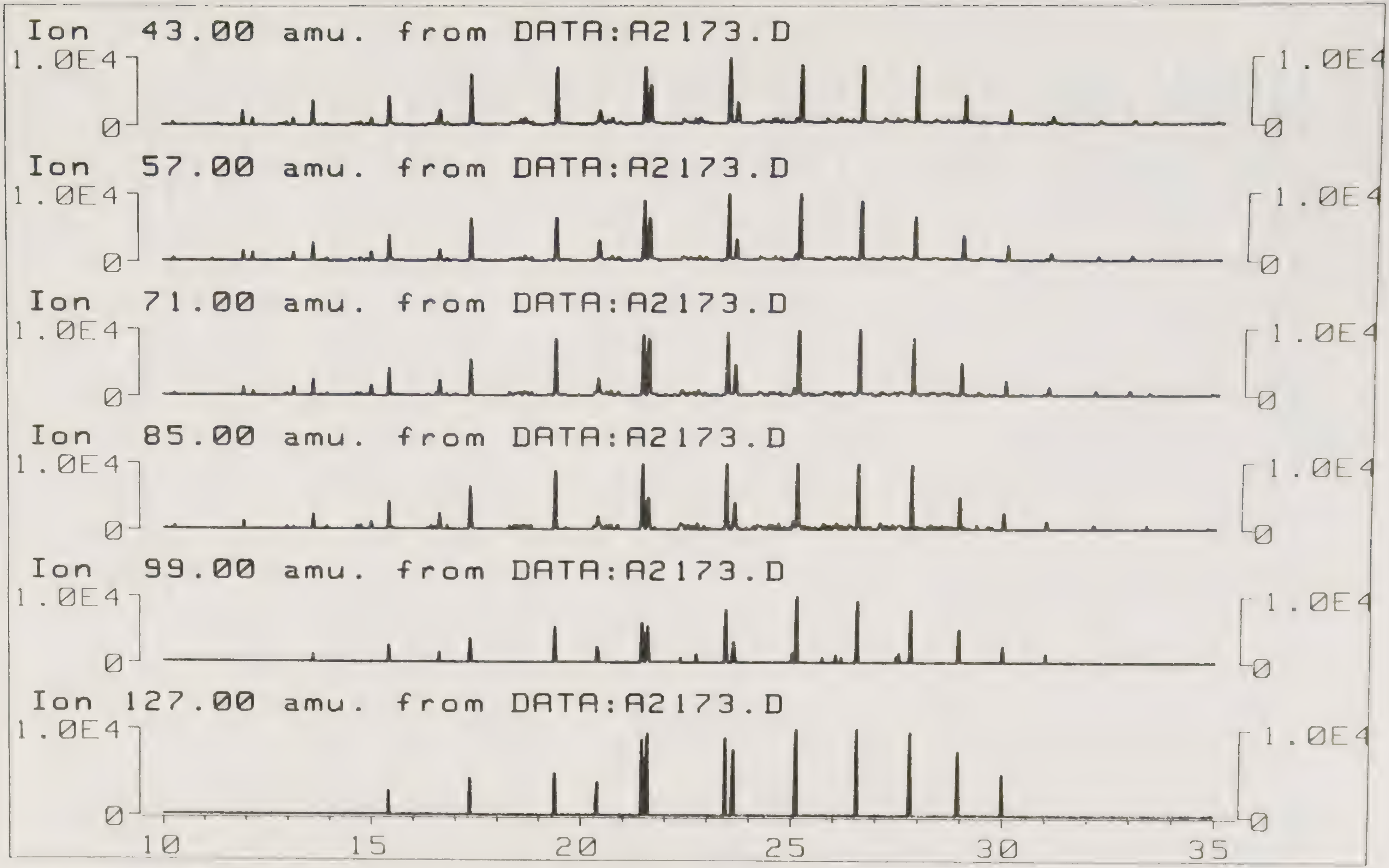


FIG 3 ION MASS CHROMATOGRAM OF A DRUM SAMPLE

Analysis of a hexane extract of a soil sample is the second example. The sample was collected near drums used to store chemicals at a supplier in Emeryville, California. Initial screening of the extract on two capillary GC columns, OV-1701 and DB-5, with election capture detectors indicated the tentative presence of several compounds related to 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (DDT). The extract was initially examined by GC/MSD using total ion scanning. The total ion chromatogram (TIC) showed a series of peaks superimposed on a broad background which is typical of many waste samples. The retention time of one major peak corresponded closely with that of a target compound, but the mass spectrum after background substraction did not match well with the reference spectrum. This is a common occurrence when analyzing hazardous wastes. Although a background spectrum can be subtracted, the resulting spectrum may not accurately represent a single compound if the levels of the background and the peak are similar or if several compounds are coeluting.

The hexane extract was analyzed by GC/MSD with using the SIM mode of data acquisition to eliminate the background. From 25.0 to 28.5 minutes three ions with m/z values of 246, 248, and 318 amu were used to monitor for 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (p,p'-DDE) and o,p'-DDE. The three ions with m/z of 235, 237, and 165 amu were used from 28.5 to 35 minutes to monitor for 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (p,p'-DDD), o,p'-DDD, p,p'-DDT and o,p'-DDT. The chromatogram based on the monitored ions contained three peaks. The retention times corresponded to those for three of the target compounds. The scan and SIM chromatograms are shown in Figure 4. The simultaneous appearance of the three characteristic ions at the proper retention times indicated that the extract contained p,p'-DDE, o,p'-DDD, and p,p'-DDD. The extracted ion chromatograms are shown in Fig. 5.

DETECTION LIMITS - MASS SELECTIVE DETECTOR

Several approaches have been reported for determining a limit of detection (9). A commonly used method is based on the signal to noise ratio (S/N). The limit of detection is the amount (or concentration) of analyte that results in a S/N sufficient to provide a level of confidence that the amount (or concentration) measured is statistically different from the analytical blank. Usually a S/N of 3 is believed to be adequate (10). For this study S/N was measured by a macro program supplied with the MSD software.

The limit of detection for scan and SIM data acquisitions with the MSD was determined for six compounds, the o,p' and p,p' isomers of DDE, DDD, and DDT. The S/N for scan acquisition was 3.7 for pp'-DDT at 0.5 ppm. As illustrated in Figure 6, the "noise" was found to be mainly ions with m/z values less than 160. The S/N increased to 1.5×10^2 when the extracted ion chromatogram included the mass range of 160 to 320 amu.

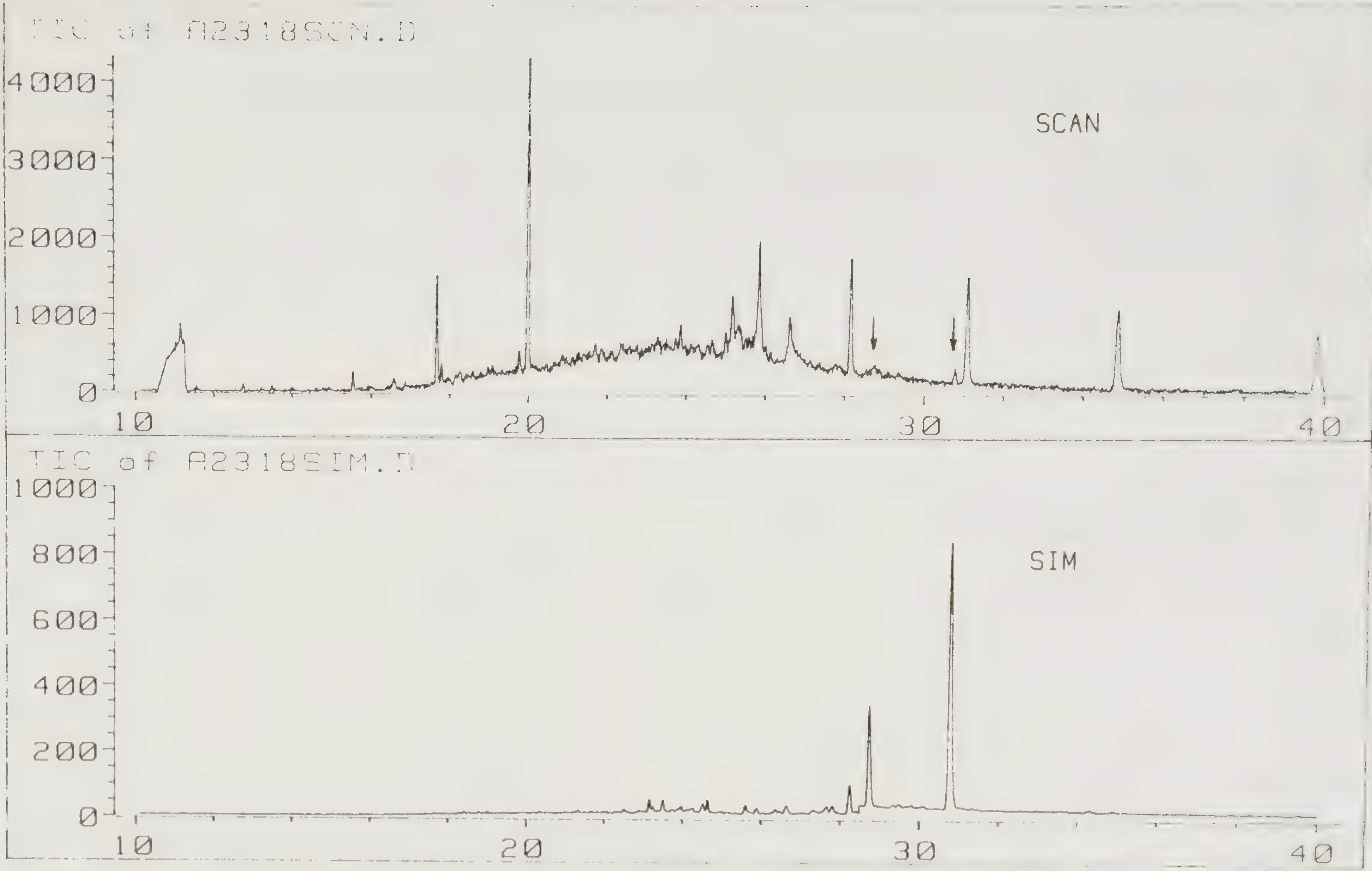


FIGURE 4 SCAN AND SIM CHROMATOGRAMS OF SOIL EXTRACT

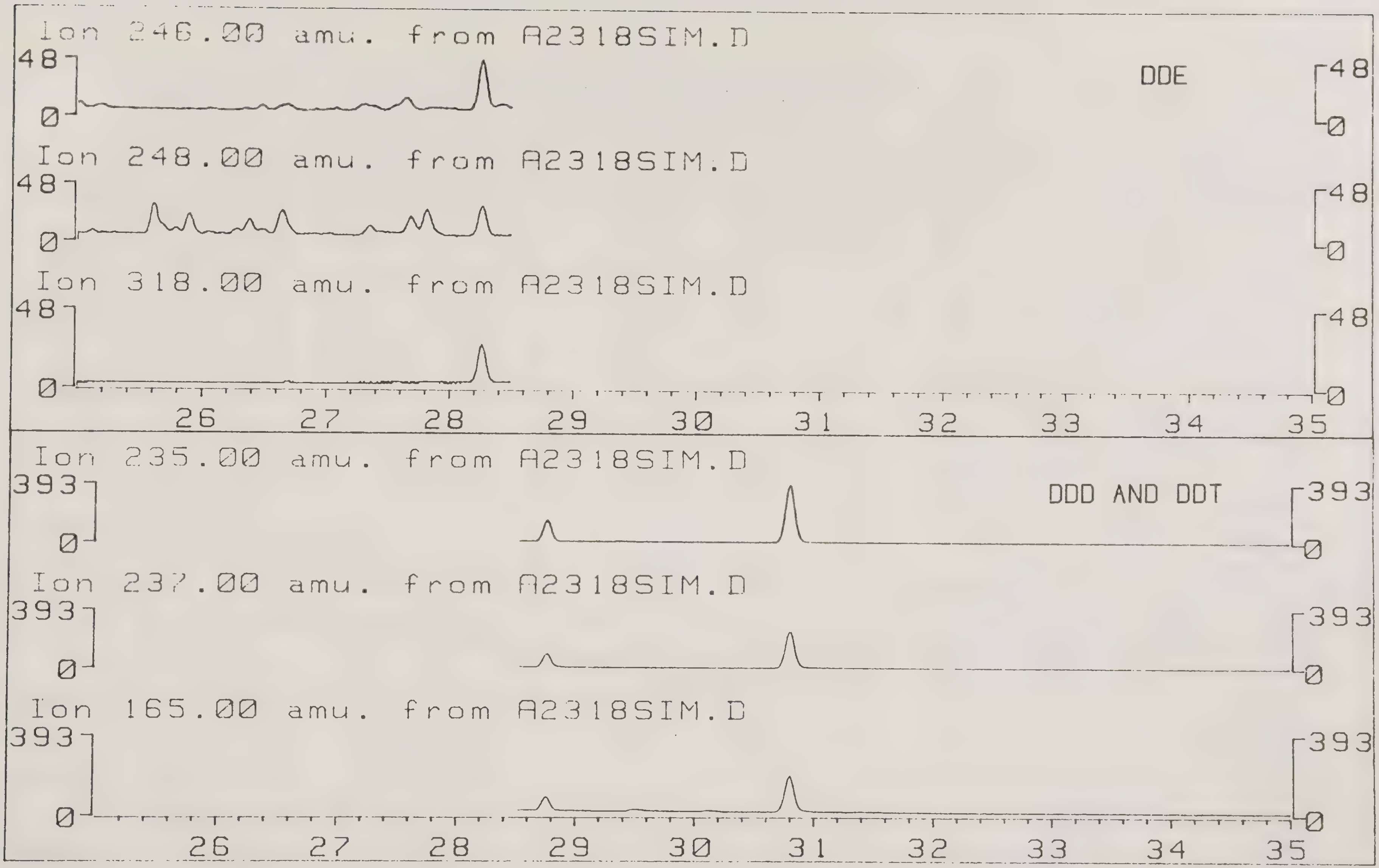
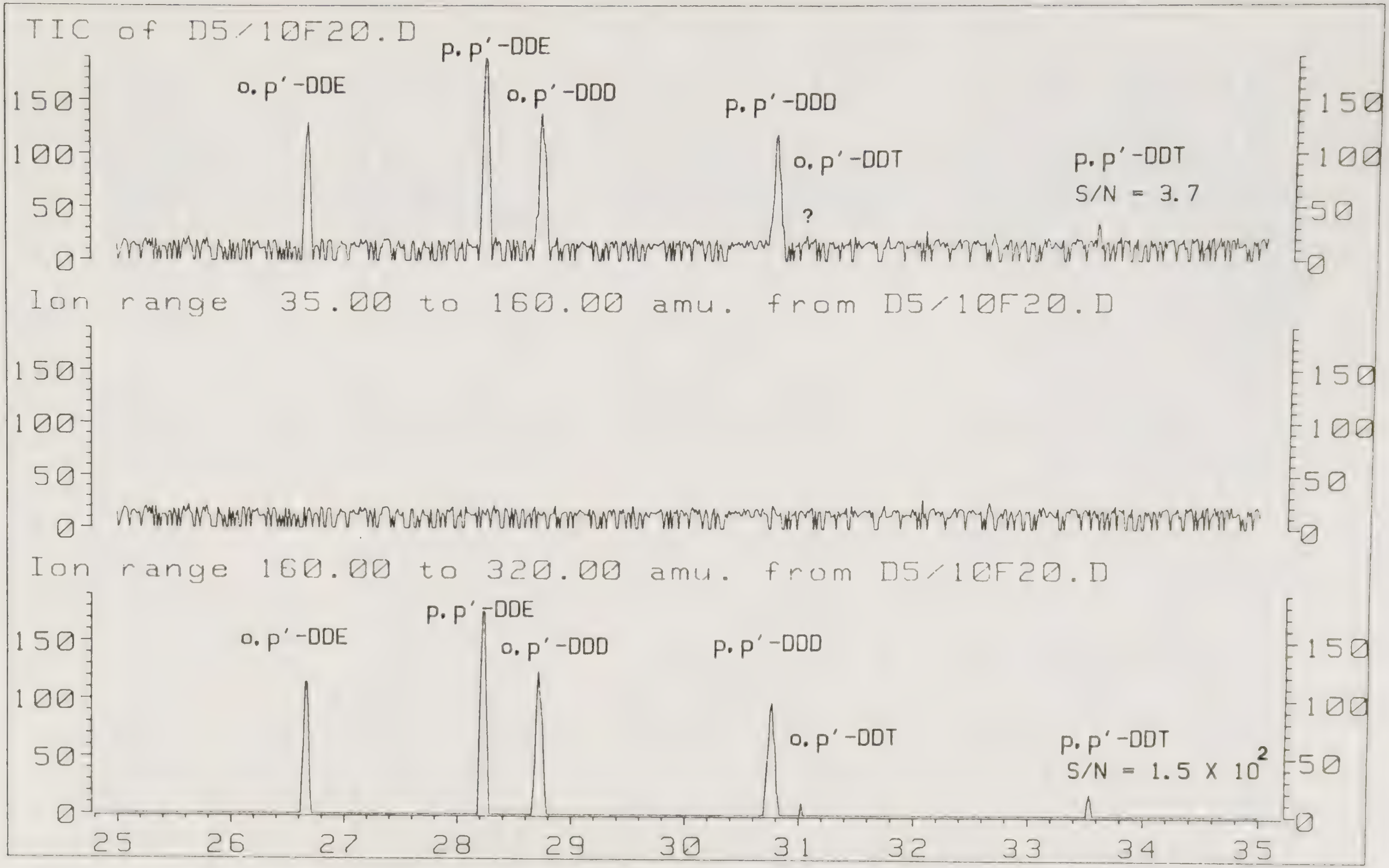


FIGURE 5 CHROMATOGRAM OF CHARACTERISTIC IONS FOR DDE DDD AND DDT



NOTE: 0.5 PPM WITH INJECTION VOLUMN OF 2 UL

FIGURE 6 TOTAL AND ION RANGE CHROMATOGRAMS OF DDE, DDD AND DDT (SCAN)

Figure 7 shows chromatograms of the mixture at 0.1 ppm, which were acquired by scan and SIM. The ions monitored by SIM were the six shown in Figure 5 for the analysis of sample A2318. Various parameters were adjusted to maximize the SIM response. These included selecting optional dwell times, calibrating the monitored ions to 0.1 amu, tuning the detector voltages, and increasing the average mass peak width. Two particularly effective techniques to maximize response were to tune the MSD to three PFTBA ions with m/z values close to the ions monitored and to use low MS resolution to increase the average mass peak width. Table 4 is a summary of the S/N ratios for scan and SIM acquisition at various concentrations. In the scan mode the limit of detection for p,p'-DDE was 0.4 ng and for p,p'-DDT was 1 ng. For SIM acquisition the limits of detection were approximately two orders of magnitude lower; 10 pg for p,p'-DDE, 4 pg for p,p'-DDD and 20 pg for p,p'-DDT.

SUMMARY AND CONCLUSIONS

A comparative study of analyses performed on a Finnigan 4500 mass spectrometer and a Hewlett Packard 5790 mass selective detector was made. The average variation in concentration levels found by the two instruments was 14% for acids and 23% for base/neutrals. Positive compound identification by the MSD was achieved by comparison of retention time and full scan mass spectrum with those of reference compound. Based on these results, the Laboratory Certification Division of this laboratory has approved the GC/MSD as an acceptable system for analysis of semivolatile organics in hazardous wastes. Applicable classes of organics include acids, base/neutrals and pesticides.

Other MSD features, which are useful for analysis of hazardous wastes were examined. Macro programs were developed to provide semi-automated screening for target priority pollutants. Studies with SIM acquisition demonstrated enhanced detection limits of target compounds in standard mixtures and in the presence of contaminants. SIM acquisition also provided potential quantitation. However, reliable library search and comparison of mass spectra is not possible with the limited number of ions from SIM acquisition. The reliability of identification should be improved if the abundance ratio of monitored ions is considered.

In summary, the MSD was found to be an attractive alternative to more costly systems for the analysis of hazardous wastes.

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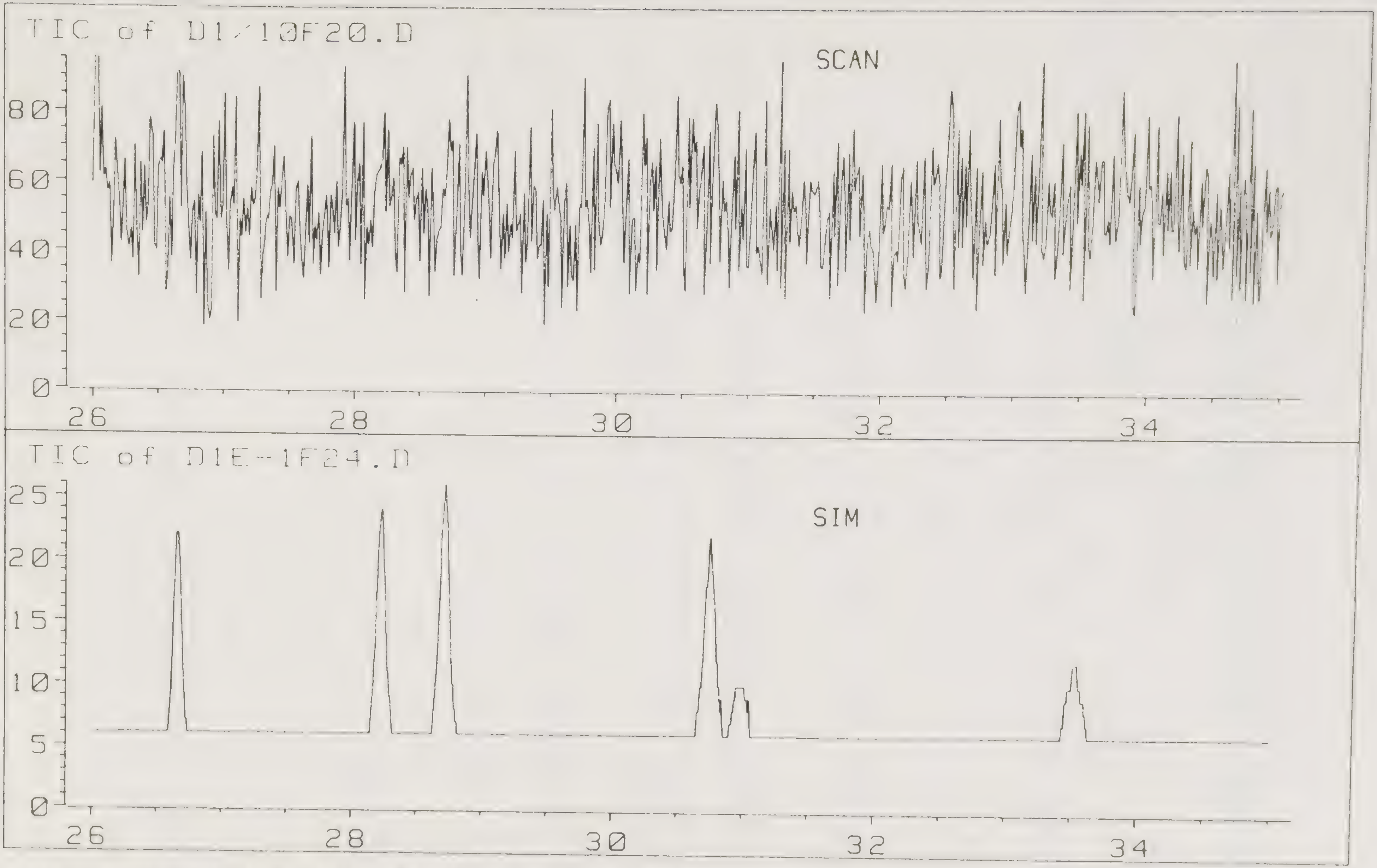

NOTE: 0.1 PPM WITH INJECTION VOLUMN OF 2 UL

FIGURE 7 CHROMATOGRAMS OF DDE DDD AND DDT

TABLE 4A - S/N FOR DETECTION OF DDE, DDD, AND DDT BY SCAN ACQUISITION

CONCENTRATION (PPM)	THRESHOLD	S/N p,p' - DDE	p,p' - DDD	p,p' - DDT
1.0	10			9.8
0.5	10	41	24	3.7
0.5	5	20	11	<3
0.2	10	4	<3	<3

Conditions: Autotune, EM = 1600 V, Injection Vol. = 2 μL

TABLE 4B - S/N FOR DETECTION OF DDE, DDD, AND DDT BY SIM ACQUISITION

CONCENTRATION (PPM)	EM (volts)	TUNE FILE	S/N p,p' - DDE	p,p' - DDD	p,p' - DDT
0.02	1600	Auto	1×10^2	1×10^2	ND
0.01	1600	Auto	ND	ND	ND
0.02	1600	User	3×10^2	3×10^2	1×10^2
0.02	1800	User		19	9.5
0.01	1800	User	9.1	12	4.3
0.005	1800	User	4.9	5.7	<3
0.002	1800	User	<3	4	<3

Conditions: Dwell = 50 msec, low MS resolution, injection vol. = 2 μL

ND = not detected

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USE OF SOIL GAS SURVEYS FOR OPTIMIZATION OF MONITORING WELL PLACEMENT

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ABSTRACT

Shallow soil gas surveys were conducted at two known organic chemical spill locations to assess the approximate extent of volatile organic chemicals (VOCs) in the subsurface. Soil gas samples were removed, under negative pressure, from the subsurface and were analyzed in the field using a portable organic vapor analyzer (OVA) and a field-operable laboratory-grade gas chromatograph (GC). The results of these surveys indicated that the OVA was more useful for the detection of VOCs in situations where the organic chemical sources were well defined and contaminants were present on the soil gas at relatively high concentrations. The GC was more useful in situations where the location of the volatile organic chemical source was not well known and/or where the soil gas contaminant concentrations were relatively low. Both soil gas survey techniques were found to be valuable preliminary assessment tools, allowing large areas of suspected contamination to be surveyed in a fast, inexpensive, and environmentally nondisruptive manner. Because the data were analyzed in the field, the results of each probe were available, almost immediately, to further guide the survey. This allowed the survey to progress in an efficient manner with a minimal number of sampling locations. This information can be used to optimize the placement of groundwater monitoring wells and soil borings.

Introduction

The soil gas survey technique is based on the premise that many VOCs will volatilize from contaminated groundwater and soils. The VOCs will move as gases (gas phase) by molecular diffusion away from source areas, toward regions of lower concentration in the overlying soil. At sites where groundwater containing VOC's has migrated away from source areas, the concentration of VOCs found in the gaseous component of the vadose zone may be related, in a general way, to the concentration of VOCs found in the aqueous phase below [1,2]. Soil gas sampling is used to attempt to identify areas of high soil gas concentrations, surrounded by lower soil gas concentrations, as a means of broadly delineating the zones of groundwater and soils containing volatile constituents. Used

in this way, soil gas sampling is an effective, relatively non-disruptive technique to quickly identify the general extent of sub-surface materials containing elevated levels of VOCs. This information can then be used to effectively locate the placement of groundwater observation wells and soil borings for more detailed site characterization.

Sampling and Analytical Methods

In the two examples discussed in this paper, samples were analyzed on site for bulk VOCs and, at selected locations, for six specific constituents: Benzene (Bz), Toluene (Tol), Methyl ethyl ketone (MEK), Xylenes (Xyl), Trichloroethylene (TCE), and Perchloroethylene (PCE).

Bulk VOCs were analyzed using a Foxboro 128 Organic Vapor Analyzer (OVA) with a flame ionization detector (FID). This was accomplished by driving probes, perforated over the bottom 9 inches and made of 1/2-inch galvanized steel, to depths of approximately 4-1/2 feet. A suction pump connected to the probe removed the subsurface soil vapor, which was continuously monitored by the OVA at the surface. Readings were recorded at 5 and/or 10 minutes after pumping began. This procedure allowed several pipe volumes to be evacuated before sampling began. The detection limit for the OVA was approximately 1 ppm, under good conditions. For conditions where emissions from cars and nearby exhaust fans raised the background levels, the detection limit was 3 to 5 ppm.

Based on the results of the sampling of bulk VOCs, selected probes were resampled a few days later using a Field Operable Varian 3700 Gas Chromatograph (GC). This was done to gain further information on the nature of the constituents and the number of contamination sources. In addition, because the GC is more sensitive than the OVA, lower concentrations of contaminants could be detected. Samples were collected using the same sampling system as for bulk VOCs, with the exception that samples were collected with a syringe through a membrane (septum) in the sampling line and were then injected directly into the GC for analysis.

The GC used was equipped with both a flame ionization detector (FID) and an electron capture detector (ECD). These detectors provide detection limits down to approximately 0.08 parts per million (ppm) for benzene, toluene, methyl ethyl ketone, xylene, trichloroethylene, and perchloroethylene, with the FID, and approximately 0.1 parts per billion (ppb) for trichloroethylene and perchloroethylene, with the ECD. Samples collected 5 to 7 minutes after pumping began were usually analyzed simultaneously on both detectors using identically packed columns.

Probes were installed by making small holes through the concrete, asphalt pavement, or grass, and driving the probes with a post driver to approximately 4 1/2 feet below the surface.

Geological Setting and Brief Site Histories

The two sites considered here are located within miles of each other in southern California and are underlaid by similar sediments. The primary geologic units were foundation fill materials, to several feet depth, overlying Pleistocene marine terrace deposits. These deposits consist of silts, fine sands, and coarse sands interlayered with clay lenses, which are sometimes several feet thick. These clay lenses may serve locally as the upper boundaries to locally confined aquifers that appear to be limited in both vertical and horizontal extent.

Both sites are locations where solvents had been used for over 10 years. Site I consisted of an asphalt covered area approximately 200 x 400 feet, bordered by a large grassy area to the east. Contamination was suspected from a small (3 x 4 foot area) unlined basin that was known to have leaked, but was no longer being used (Figure 1 - point A). Another area of concern at this site was a location that was currently being used for drum storage and for cleaning activities (Figure 1 - point B). Historically, several other areas had been used, at various times in the past, for both drum storage and/or cleaning activities. The exact locations and times for these activities were unknown. As a result of preliminary sampling, it appeared that quantities of several solvents had been used at the site.

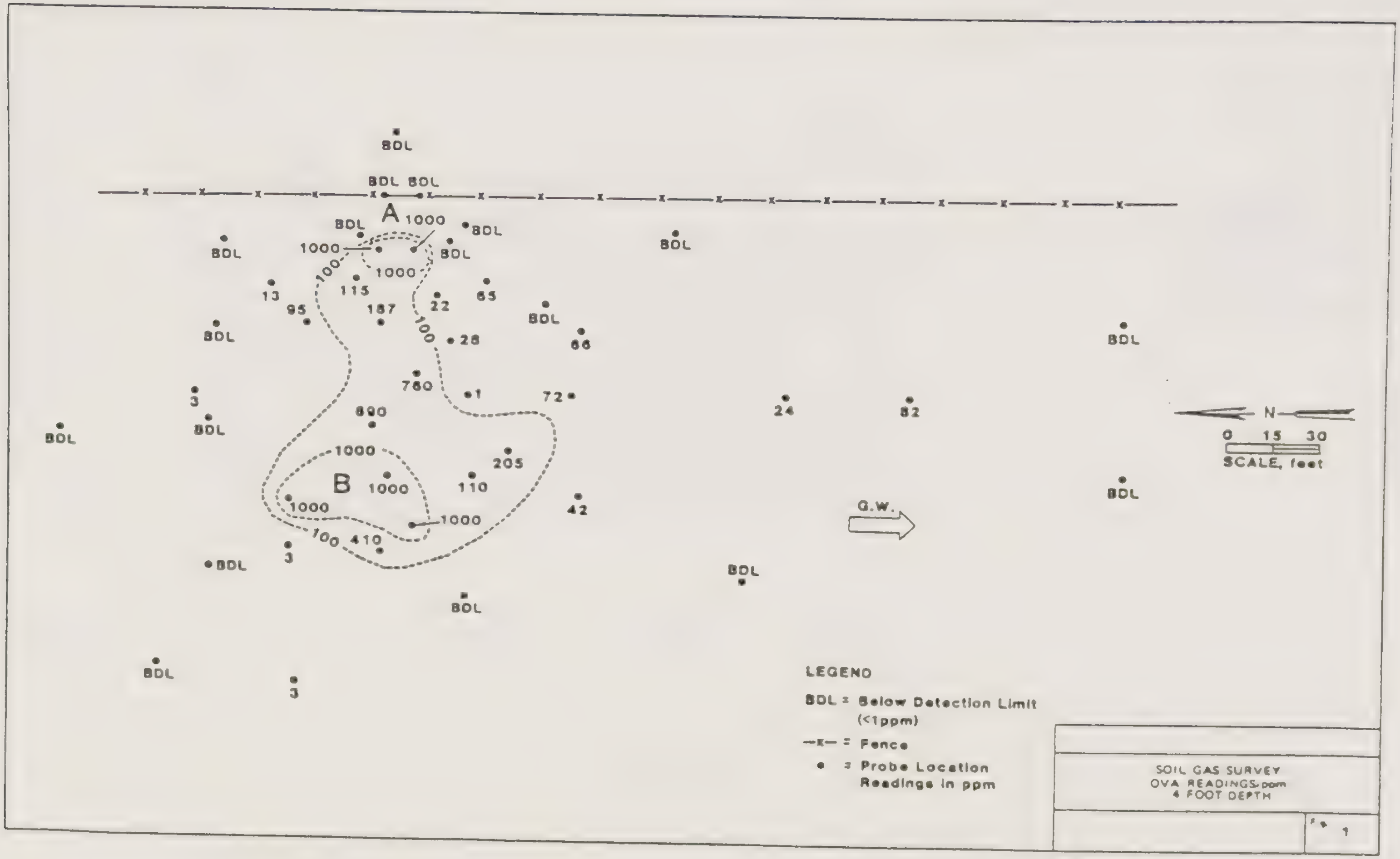
Site II was approximately 700 x 1200 feet. Most of the site is covered with two large buildings and asphalt parking areas. Some access to the soil gas was made through planters located in the parking areas. Contamination was suspected from abandoned solvent basins at three locations in the buildings (Figure 3 - points A, B, and C). Each of these basins covered an area of approximately 10 x 20 feet. Another area of concern was an area previously used for the storage of solvents (Figure 3 - point D). The main identified constituents were TCE and PCE, with only minor amounts of nonhalogenated compounds.

Hydraulic gradients, based on data from wells in the areas near the sites, were interpreted to be to the south at Site I and to the west at Site II.

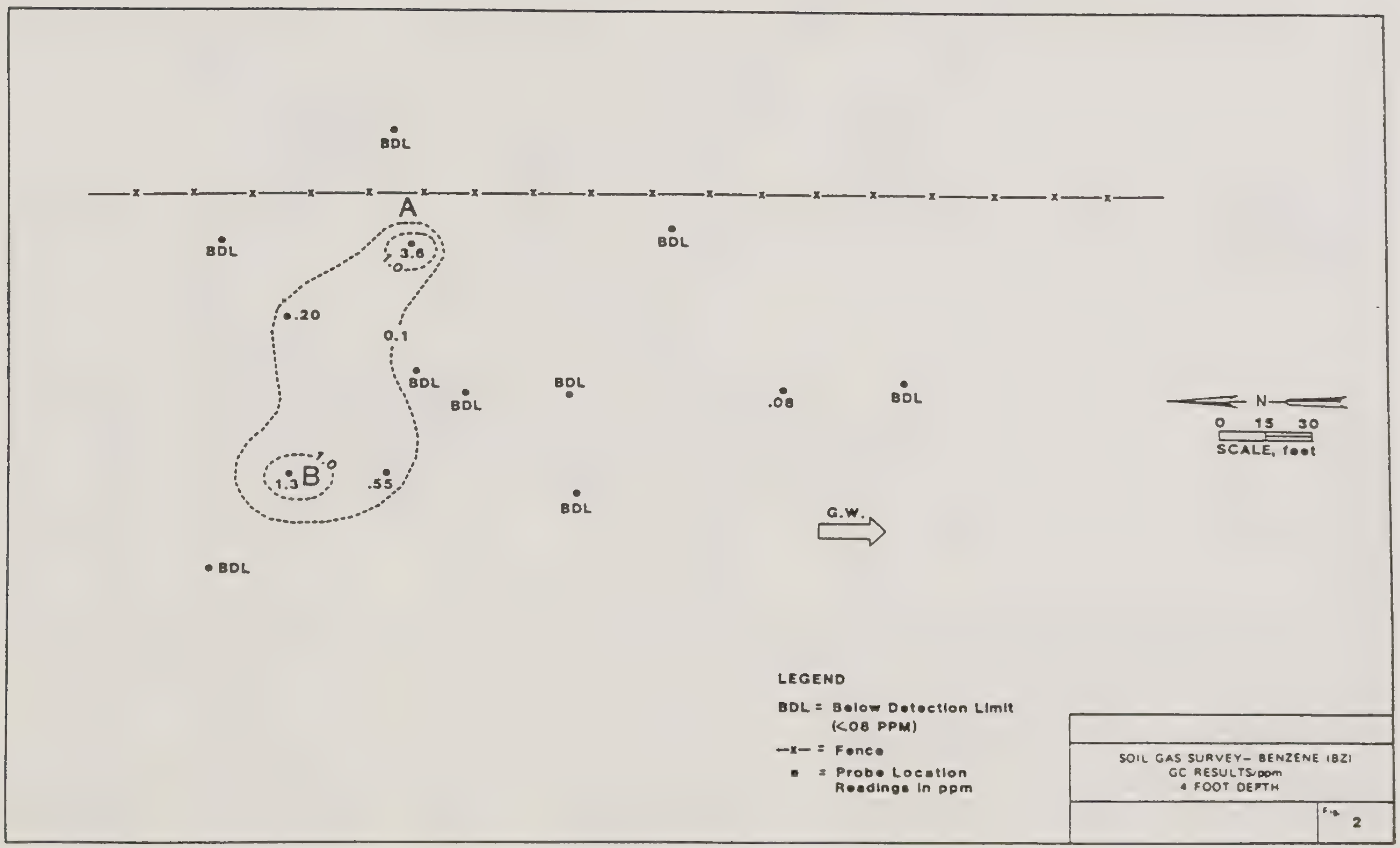
Results

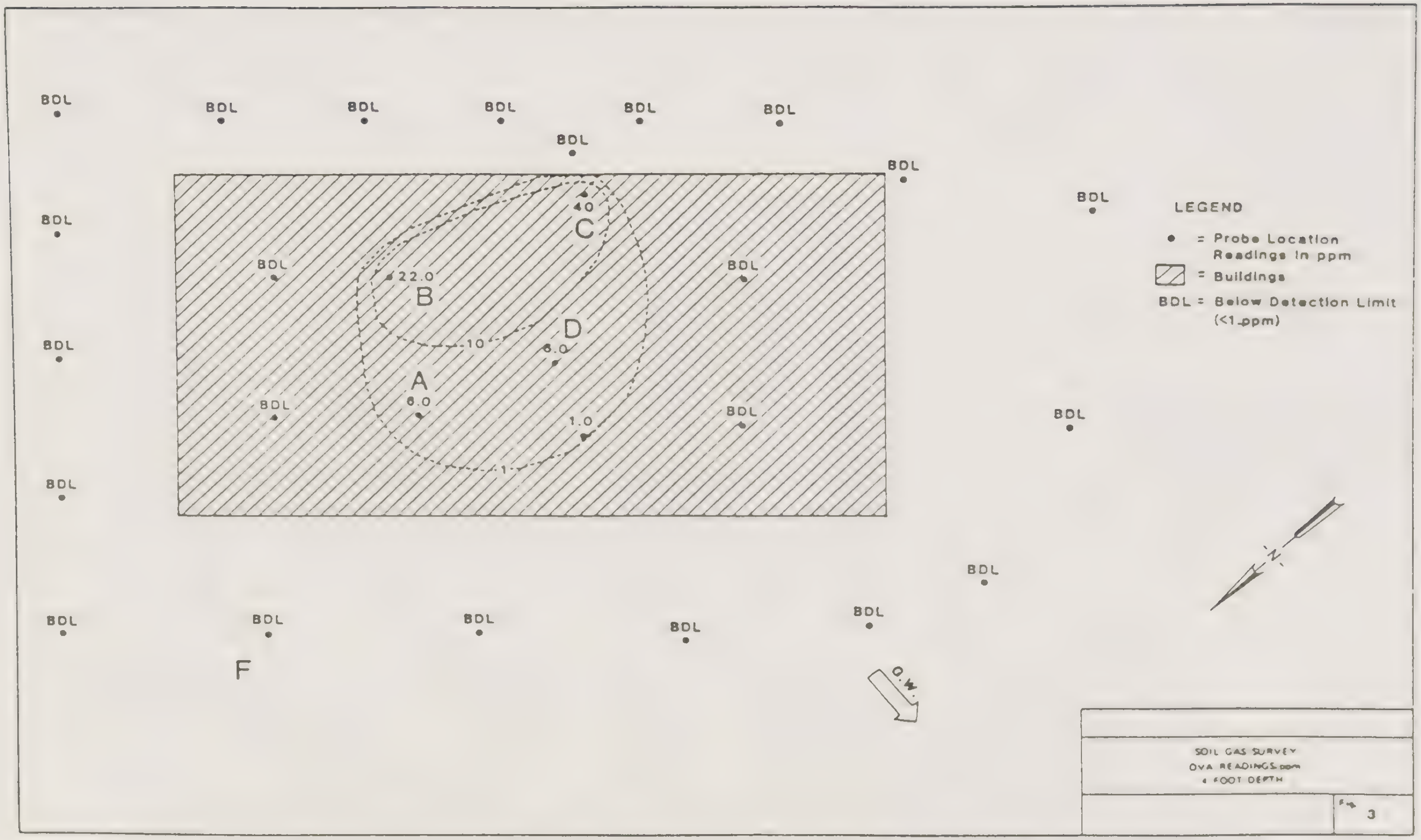
While six constituents were identified and measured at each site, for discussion purposes, only the Benzene (Bz) concentrations are reported for Site I and the Trichloroethylene (TCE) for Site II. In general, the trends of concentrations for the two compounds discussed here match the trends seen in the other four compounds.

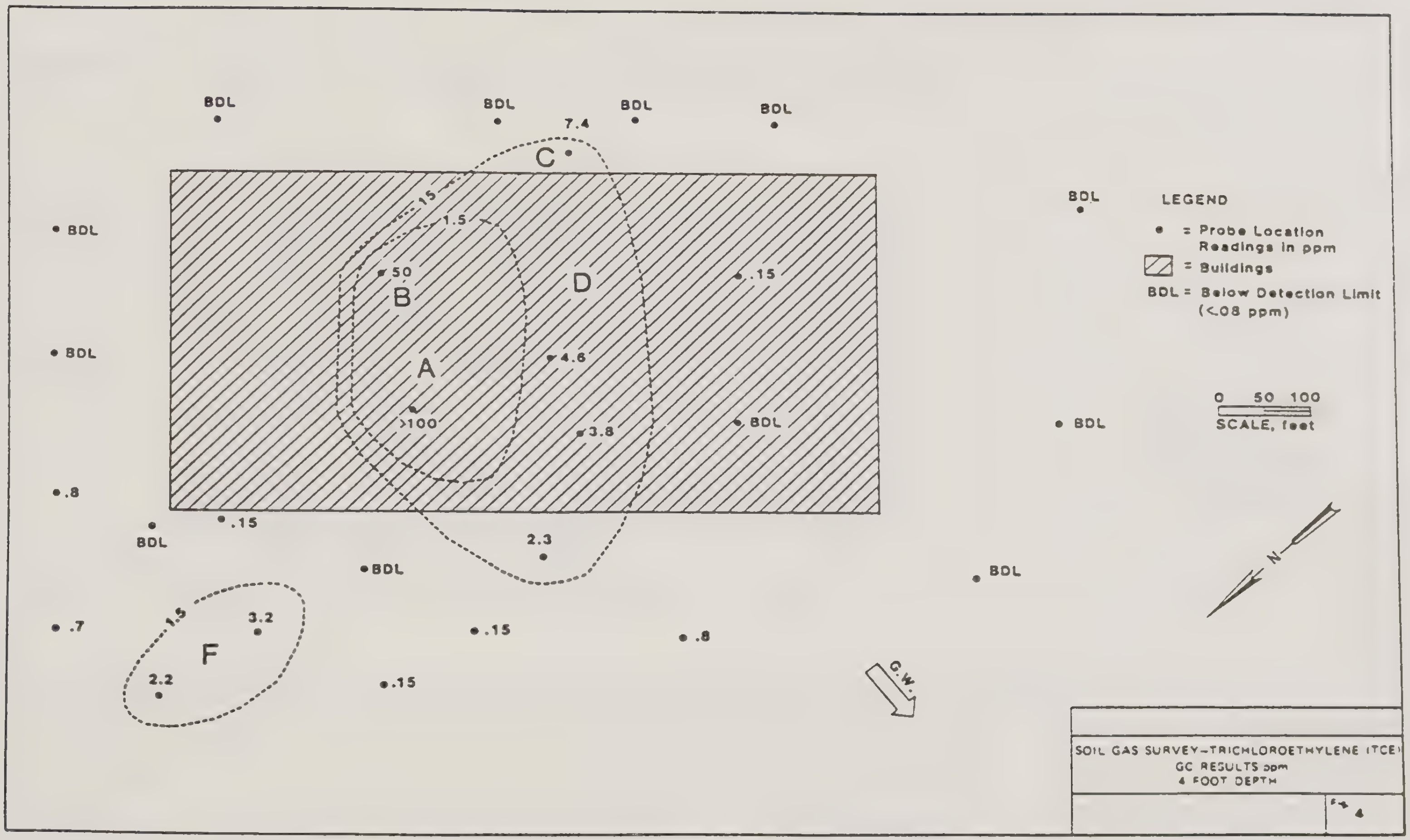
Figures 1 through 4 show the probe locations, the individual probe readings, and the contoured data. Figures 1 and 3 depict OVA readings for Site I and Site II respectively. Figures 2 and 4 similarly refer to



A
B
G.W.
N
0 15 30
SCALE, feet
LEGEND
BDL = Below Detection Limit (<1ppm)
—x— = Fence
• = Probe Location Readings in ppm
SOIL GAS SURVEY
OVA READINGS, ppm
4 FOOT DEPTH


BDL
A
BDL
BDL
3.6
1.0
.20
0.1
BDL
BDL
BDL
.08
BDL
N
0 15 30
SCALE, feet
1.0
1.3 B
.55
BDL
G.W.
BDL
LEGEND
BDL = Below Detection Limit (<.08 PPM)
—x— = Fence
■ = Probe Location Readings in ppm
SOIL GAS SURVEY– BENZENE (BZ)
GC RESULTS/ppm
4 FOOT DEPTH
Fig. 2


BDL
22.0
B
40
C
D
6.0
A
6.0
1.0
10
1
F
LEGEND
• = Probe Location Readings in ppm
= Buildings
BDL = Below Detection Limit (<1 ppm)
N
G.W.
SOIL GAS SURVEY
OVA READINGS ppm
4 FOOT DEPTH
3


BDL
7.4
C
1.5
1.5
50
B
D
.15
A
4.6
>100
3.8
BDL
.8
.15
2.3
F
3.2
2.2
.7
.15
.8
G.W.
N
LEGEND
• = Probe Location Readings in ppm
= Buildings
BDL = Below Detection Limit (<.08 ppm)
0 50 100
SCALE, feet
SOIL GAS SURVEY–TRICHLOROETHYLENE (TCE)
GC RESULTS ppm
4 FOOT DEPTH

the reported constituent from the GC analyses for Site I and Site II, respectively.

For the sake of consistency and simplicity, all results reported are from the FID detector. Hydraulic gradients are indicated with the arrow marked GW.

Soil Gas Survey Evaluation

Figure 1 shows the results of the OVA survey conducted at Site I. When originally proposed, the investigation was concerned with discovering the extent of possible contamination from an area suspected to be contaminated from the leaky solvent basin, indicated as source A. However, after a few preliminary probes, the apparent existence of a second possible source became evident, at or near the areas currently used for cleaning (source location B), and the sampling program was expanded to include a larger area. Probes were emplaced in all quadrants away from the areas of high concentration at more or less regular intervals until concentrations were no longer detectable with the OVA. Following the OVA survey, the GC analysis phase of the investigation was undertaken to identify the individual constituents. Figure 2 shows the results in terms of the benzene concentrations. Overall, the trends in the OVA readings correspond with the trends of the GC readings. In terms of overall concentrations, the benzene concentrations are approximately 0.1 percent of the total measured by the OVA.

Based on information gained during the soil gas surveys, the contaminated area appeared to be more or less limited to areas immediately surrounding the two apparent sources. This information was useful in that the probable extent of the contamination was shown to be more limited than originally suspected.

At Site II, the OVA readings (Figure 3) were interpreted to indicate broad areas of high concentrations beneath the buildings, with the higher concentrations occurring at or near points B and C. In areas surrounding the buildings, concentrations were uniformly low. As previously mentioned, the background for the OVA varied from 1 to 5 ppm, depending on the amount of VOCs that were in the ambient air. Figure 4 depicts the concentrations of TCE as measured by the GC. For the most part, the high concentration areas identified with the OVA corresponded with high concentrations of TCE except for several of the probes in the northeastern portion of the study area near point F; TCE concentrations observed there were, for the most part, below the background levels obtainable with the OVA. The area of contamination at point F was not predicted on the basis of the available hydraulic gradient. Indeed monitoring well locations selected on the basis of information about the gradient would have probably missed these areas of high concentration. Overall TCE concentrations are approximately 40 percent of the total VOC concentrations measured at Site II.

Our experience indicates that apparent inconsistencies, or short distance variability, in the soil gas readings should not be interpreted too strictly. Local variations in the permeabilities of subsurface materials may result in readings that are locally higher or lower than adjacent probes. Instead trends in the data, involving two or more probes, should be noted.

Summary

Both OVA and GC soil gas survey techniques provide relatively inexpensive, environmentally non-disruptive methods to quickly identify areas of high VOC concentration. At Site I, high concentrations of VOCs that were apparently limited in extent, were, for the most part, detected equally well by either of the survey techniques. At Site II, where concentrations were lower and where migration may have occurred, the GC was more useful for detecting elevated concentrations. Both methods can be a valuable aid in optimizing the placement of soil borings and/or groundwater monitoring wells.

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ACKNOWLEDGEMENTS

Special thanks to Kevin Gibson who performed a large part of OVA soil gas work and Nilmini Silva who assisted with the GC analyses. My gratitude to Alistaire Callender and George Linkletter who reviewed the paper and offered many useful suggestions.

ABSTRACT:

VAPOR MONITORING: A RAPID, LOW COST ALTERNATIVE FOR UNDERGROUND CONTAMINANT PLUME DELINEATION

BY
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IT CORPORATION, MARTINEZ, CALIFORNIA 94553

Rapid delineation of the extent of subsurface, volatile, and semi-volatile contaminant plumes is of utmost importance in urban and suburban environments. These plumes have the potential to contaminate the ground water, and also present a significant safety hazard. Flammable vapors may concentrate in enclosed spaces, causing serious health, fire, or explosive hazards.

Vapor monitoring can provide timely information about the location of subsurface volatile and sub-volatile contaminant plumes. In contrast to traditional drilling methods, measurements of vapor concentrations can be made from a large number of hand drilled borings in a relatively short amount of time.

Drilling monitoring wells is more costly and much slower. Usually only four to five wells can be installed in one day. This limitation causes the time frame for adequate delineation of the contaminant plume to expand, hence increasing the cost of the preliminary investigation. In addition, the large equipment used for drilling causes access and traffic difficulties at suburban and urban sites. Finally, the expense of a drill rig and crew is far greater than the cost of the crew necessary for a vapor monitoring survey.

The following case study illustrates the effectiveness and applicability of vapor monitoring. The study area is characterized by dry sandy soil and a relatively shallow ground water table. Migration of gasoline into an underground utilities vault caused serious damage to cable transmitting equipment. Gasoline vapors in the vault presented a serious health and fire hazard to the public. Nearby gasoline service stations were the apparent source of this contamination.

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*Proposed for presentation at the HAZMACON '86 Conference, Anaheim, California April 29-May 1, 1986

Vapor monitoring through eighteen holes drilled in the adjacent streets to a depth of 3.5 feet successfully delineated the lateral extent of the vapor plume. This plume was defined to an area adjacent to one of the gasoline service stations, thereby providing strong circumstantial evidence as to the source of the contaminant plume.

The boring and vapor monitoring took approximately six hours and did not require significant traffic disruption. Further, the extent and location of the vapor plume was delineated in the field that afternoon. In contrast, drilling a sufficient number of monitoring wells to delineate the contaminant plume would have required at least two days. Additional difficulties were that monitoring wells would have been located in major street intersections, presenting serious traffic and safety hazards.

This study demonstrated that vapor probe monitoring is a fast, cost-effective method for locating a subsurface vapor plume. This method is effective in clean, dry sands. The effectiveness is diminished in soils with high clay contents or soils with high moisture content.

As demonstrated by this study, vapor monitoring is a valuable method for reconnaissance delineation of a vapor plume. However, further investigation of a plume identified using this method may require the installation of a ground water monitoring wells to provide continued information on the location of the vapor plume, its source, the semi-volatile and volatile compounds generating the plume, and a remediation plan.

VAPOR MONITORING: A RAPID, LOW COST ALTERNATIVE FOR UNDERGROUND CONTAMINANT PLUME DELINEATION

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INTRODUCTION

Vapor monitoring provides a rapid, cost effective method of delineating subsurface vapor plumes under appropriate soil conditions. Traditional drilling methods are more expensive and time consuming, hence not always best for the initial delineation of a contaminant plume.

This paper presents a case study demonstrating the effectiveness of vapor monitoring under appropriate conditions. Also presented is a cost comparison between vapor monitoring and drilling methods.

Background

In this recent study, chronic presence of gasoline in an underground utility vault had caused degradation of transmitting equipment and presented a serious fire hazard. IT Corporation was retained to assess the site and proposed to conduct a vapor monitoring survey to delineate the spatial relationship of a suspected gasoline plume to the utility vault. The purpose of the study was to determine the extent of the plume with respect to connecting underground conduit, city streets, and gasoline service stations in the vicinity, as shown in Figure 1. In addition, IT also proposed to attempt to determine the source of the plume via comparative compositional chemical analysis of gasoline samples collected at the site.

The site is located at an intersection in downtown Santa Cruz, California which is in the San Lorenzo River flood plain, about 300 meters from the river (Figure 1). Soil underlying the site is dry, clean, medium sand. These soil characteristics are especially favorable to vapor monitoring (Penman, 1940).

Scope of Work

The vapor monitor survey was completed in one working day by a four-man crew consisting of an IT Scientist, a technician, and two laborers. 1.5-inch diameter holes were drilled through the intersecting streets with an air-rotary hammer to a depth of four feet. Measurements of vapor concentrations in these borings were taken using a GX-3A vapor monitoring meter immediately after drilling by inserting the probe into the boring to a depth of approximately three feet. Prior to measurements, the GX-3A was calibrated against ambient background vapor conditions. Calibration range of the GX-3A meter is 0 ppm to 1000 ppm.

Twelve boreholes were laid out in a roughly radial pattern away from the utility vault. Vapor monitoring data plotted of Figure 2 defines the areal extent of the vapor plume out into the intersection.

Hydrocarbon Source Identification

Identification of the probable hydrocarbon source was made possible by using the concentration gradient of the plume and local hydrological variance caused by pumping of the utility vault. In addition, source conclusions based on field work were supported by the results of the comparative chemical analysis. Service Station A is upslope from Service Station B, thus, a likely source for the hydrocarbon plume. However, vapor concentrations were highest along Water Street adjacent to Service Station B, as shown in Figure 2. Further, vapor concentrations decreased rapidly in the direction of Service Station A. If Service Station A were the hydrocarbon source, the measured plume concentration gradient should increase away from the utility vault, instead vapor concentration fell off rapidly in the direction from the vault to Service Station A, thus ruling out that station as a likely source.

Upon opening the vault, prominent water mark was visible on the inside vault wall, four feet from the bottom. The vault is pumped continuously to maintain the water level below the transmission cables, leaving about three inches in the vault. The four foot high water stain is the level that ground water rises in the vault when pumping is stopped. Thus, maintenance pumping of the

vault creates a cone of depression in the shallow unconfined ground water table, which in turn, influences the plume configuration and causes gasoline to flow down gradient into the vault (Figures 2 and 3).

The plume configuration, concentration gradient, and the presence of the cone of depression centered about the vault provide strong circumstantial evidence that the hydrocarbon source was Service Station B. Furthermore, independent laboratory analysis comparing gasoline samples sold at each station with gasoline collected from the vault confirmed that the vault sample was chemically very similar to gasoline sold at Station B (and did not chemically resemble gasoline sold at Station A).

Cost Comparison

In determining the appropriate response to a hazardous waste site, time constraints, health hazards, restrictive site conditions, local geology and hydrology, and the hazardous waste involved must be considered. Companies that rely on a single investigative method are likely to find its effectiveness occasionally compromised by the varied conditions found among sites. Thus, both the effectiveness of the investigation and service to the client is reduced by overreliance on one method.

Traditionally, drilling in conjunction with monitoring well installation is used to delineate contaminant plumes. However, under appropriate soil conditions, volatile plumes may be more effectively delineated by vapor monitoring. In addition, vapor monitoring is much less expensive and time consuming. The following is a narrative comparing drilling cost for a site similar to the site described in this paper.

Five monitoring wells can sometimes be completed in one day. However, fully delineating a contaminant plume with five data points is highly unlikely. In contrast, twelve vapor monitoring borings were completed in about four hours at the Santa Cruz site. In addition, significant expenses not incurred by vapor monitoring are drilling costs, soil/water collection and analysis cost, and labor cost from well development. An itemized cost comparison is presented in Tables I and II. Drilling five monitoring wells to delineated

this plume is estimated to cost $4500.00 compared to a cost of $1545.00 to complete the vapor monitoring. Since some of the monitoring wells are likely to miss the plume, clean soil and water samples would be analyzed.

Installation of monitoring wells after the plume is delineated is warranted as the next step in this study. These wells could provide data valuable in linking the vapor plume with the parent, liquid mass, as well as providing access to potentially contaminated ground water. However, as shown by this study, plume delineation by vapor monitoring provided valuable information on the configuration of the plume, which could then be used to determine the optimum location for monitoring wells.

ACKNOWLEDGEMENTS

I would like to thank IT Corporation for providing financial and logistical support for this project.

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TABLE I

DRILLING, WELL INSTALLATION, WELL DEVELOPMENT AND ANALYTICAL COSTS

Rig Time, 10 hours + 3 hours travel	$1300.00 to $1500.00
Geologist or Engineer, 14 hours x 40 per/hours	$560.00
Truck Rental	$20.00
GX-3A	$25.00
INSTALLATION OF FIVE 20-FOOT DEEP 2-INCH MONITORING WELLS	
Blank PVC, 5x10' lengths, $2.56 per/foot	$128.00
Screened PVC, 5x10' lengths, $3.64 per/foot	$182.00
End plugs, 5 x $3.83	$19.15
Christy boxes, 5 x $21.34	$106.70
Locking well caps, 5 x $31.95	$159.75
Bentonite pellets, 3 buckets x $73.49	$220.50
Bentonite powder, 1 sack x $23.96	$23.96
ANALYTICAL COSTS	
BTX for 5 soil samples	$600.00
BTX for 5 water samples	$600.00
WELL DEVELOPMENT	
Technician, 10 hours	$400.00
Estimated Total	$4321.00 to $4521.00

TABLE II

ONE DAY VAPOR MONITORING COST

Compressor and jack hammer rental	$120.00 per/day
Two technicians 14 hours x $30.00 per/hour	$840.00
Geologist or Engineer 14 hours x $40.00 per/hour	$560.00
GX-3A vapor probe	$ 25.00
Total	$1545.00

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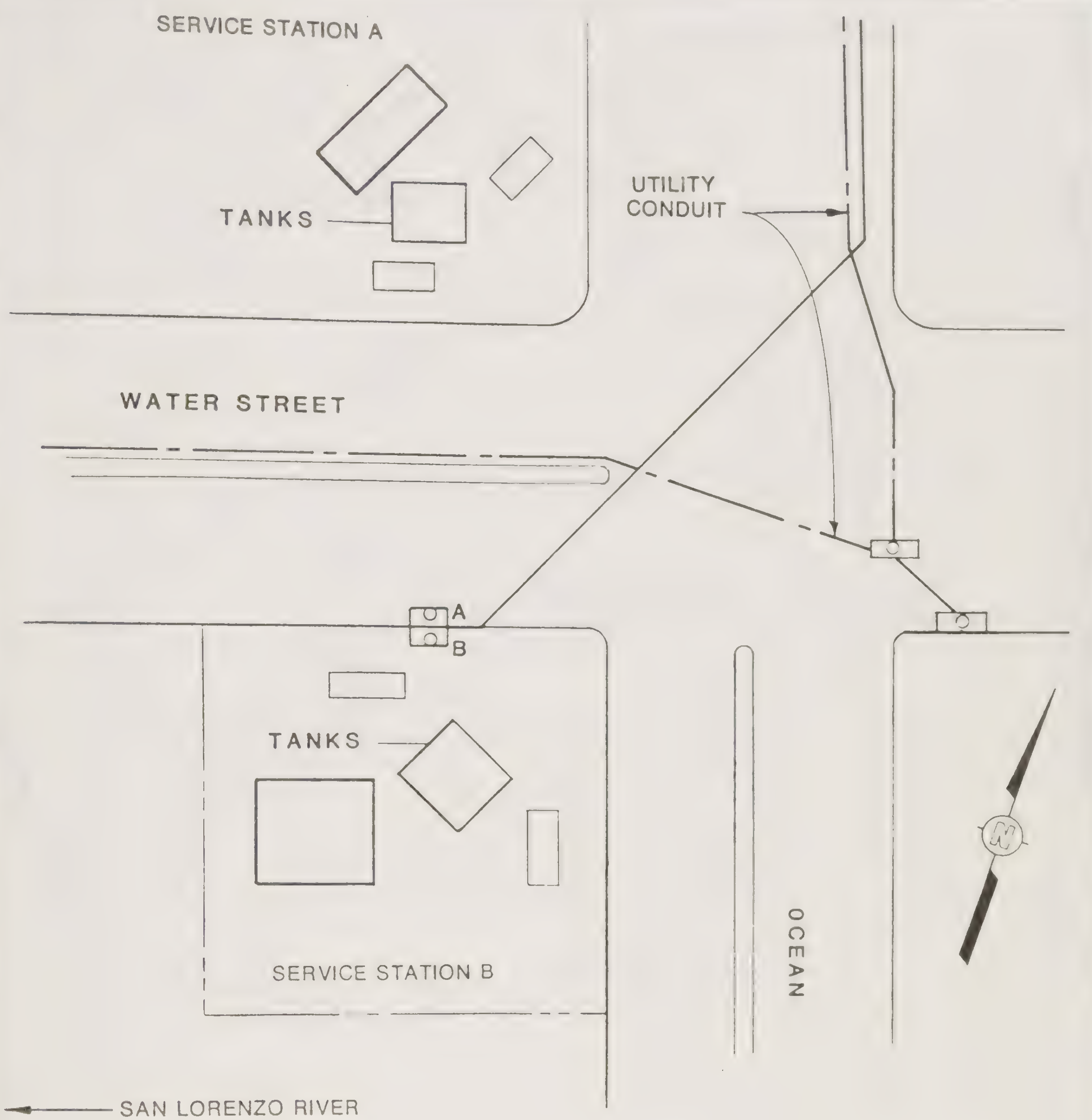

O VAULT MANWAYS

0 25′ 50′
scale

FIGURE 1
SITE MAP

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Do Not Scale This Drawing

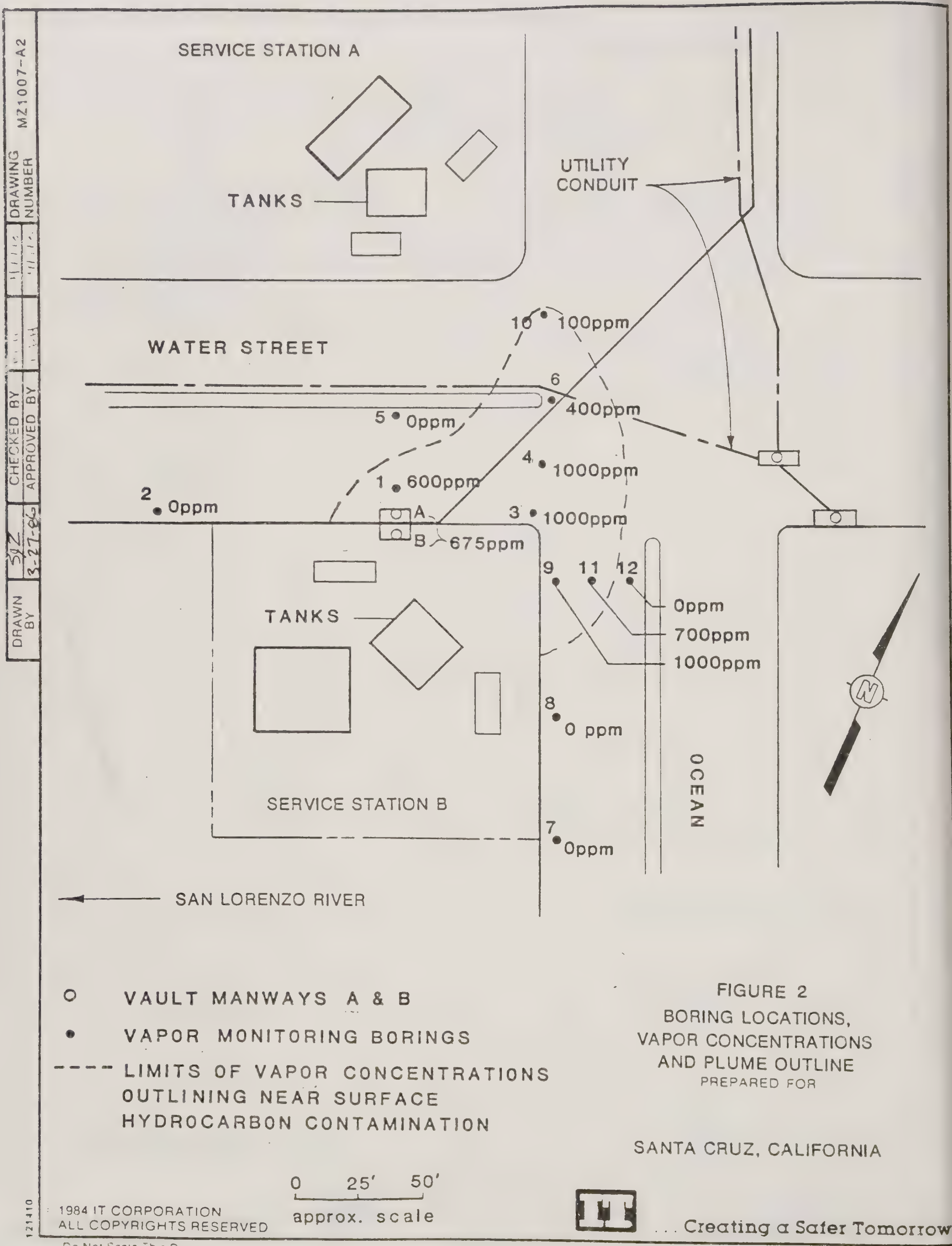

FIGURE 2
BORING LOCATIONS,
VAPOR CONCENTRATIONS
AND PLUME OUTLINE
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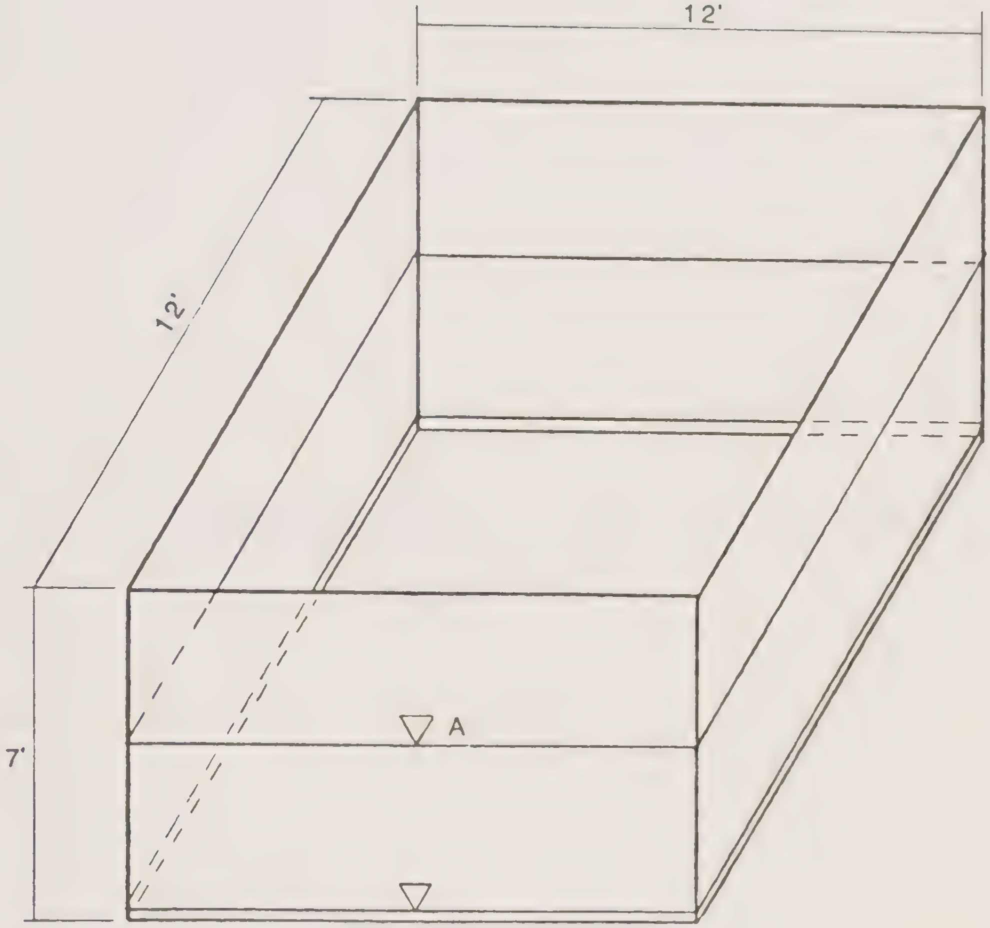

▽ A – NORMAL WATER LEVEL

▽ B – WATER LEVEL MAINTAINED BY PUMPING

0 1' 2' 3' 4'

FIGURE 3

UTILITY VAULT SCHEMATIC

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TREATMENT AND DISPOSAL

SYNERGISTIC APPROACH FOR SITING AND DESIGN FOR INJECTION OF HAZARDOUS WASTES: CASE STUDY IN WESTERN SAN JOAQUIN VALLEY, KERN COUNTY, CALIFORNIA

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Partner,
Evans, Carey & Crozier
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Susan Chandler Kiser
Consulting Geologist
Bakersfield, CA. 93301

INTRODUCTION

Subsurface injection of wastes is a technology on which a great deal has been written in last 25 years. Some of the key references are mentioned in Subsurface Wastewater Injection by Warner and Lehr (1977).

The earliest controlled waste water injection program outside of oilfield operations may have been in 1939 (Harlow, 1939 in Warner and Lehr, 1977). Its use has expanded in the last 30 years to the point that, nationally, 60% of the 15.6 billion gallons of hazardous waste legally disposed of in the U.S. is being injected through wells into deep aquifers (Gordon, 1984). In the past 30 years of hazardous waste injection, there has been a failure rate of only 2.4% (Morgan, 1986) where groundwater (either drinkable or non-drinkable) has been contaminated.

In California, commercial hazardous waste is transported to one of seven approved sites located around the state (Figure 1). None of the currently operating sites utilize deep well injection as a final disposition for Class I liquids. However, the geologic setting of the Great Valley in California was determined to be potentially suitable for deep-well waste injection by Repenning (1960) and is identified on Figure 2 from Warner and Lehr (1977). The most common form of Class II liquid disposal in California is deep well injection.

Geology and engineering requisities for successful underground injection of liquid wastes include: 1) good storage capacity of the targeted reservoir, 2) adequate confinement above and below the targeted reservoir, 3) detailed hydrogeologic understanding of the chosen site, 4) reasonable seismic stability, 5) compatibility between the liquid waste materials, the natural reservoir fluids and rock matrix, and the materials of construction, and 6) an understanding of the hydrologic effects of injection in the reservoir both short term and long term.

As an example of the methodology employed to properly select a site suitable for the injection of liquid hazardous waste, the highgrading process in site selection of TSD Systems Corporation proposed Rhetta Facility will be reviewed. The site was selected as a result of exhaustive geological, geophysical, and engineering studies conducted by a team assembled by the consulting firm of Evans, Carey and Crozier for the TSD Systems Corporation.

PRELIMINARY SITE SELECTION

The Great Valley of California had been targeted as a potential site for hazardous waste injection as previously mentioned. The study was further focused on the southern half of the Great Valley, called the San Joaquin Valley. This region has up to 25,000 feet of Tertiary sands and shales with only mild to moderate deformation. A great deal of subsurface geologic, geophysical, and engineering data in the region is available from many years of oil industry activity. All of these above reasons made the San Joaquin Valley a good place to undertake a detailed site screening process.

A preliminary review of the geologic settings, groundwater systems and land use in the San Joaquin led in the identification of four possible injection sites on the west side. These sites are bounded on the west by the outcropping permeable formations which have no confining layer, and on the east the part of San Joaquin Valley which is underlain by fresh water aquifer. The presence of fresh groundwater does not preclude the possibility of waste disposal by injection in the rest of the valley, but the poor quality groundwater on the west side was considered an added measure of desirability. All four sites in western Kern County met preliminary geologic criteria. The Antelope Plains location at Blackwells Corner also had the added benefit of being located in an isolated area not close to urbanization or the aqueduct. It is a basin not subjected to subsidence or flooding. The Blackwells Corner site was selected for a detailed geologic and engineering feasibility study.

BLACKWELLS CORNER SITE

The project site is located in a localized structural depression (Figure 3) beneath the Antelope Plain within the greater San Joaquin Valley. Subsurface structure contours on the top of the San Joaquin-Etchegoin Formations (Figure 4), delineate this depression, the flanks of which dip towards the lowest center at a slope of 3 1/2 to 4 1/2 degrees. The subsurface geology in the vicinity of the site is shown on the cross section in Figure 5. The southwest to northeast cross section, (location shown in Figure 4), runs transverse to the longitudinal direction of fold sets in the San Joaquin Valley. The boundaries of the depression are defined by the adjacent anticlines: Beer Nose to the north; North Belridge to the south; North Antelope Hills to the west; and Lost Hills to the east.

Good Storage Capacity of the Targeted Reservoir

The Pliocene San Joaquin and Etchegoin Formations have been selected as the injection zone. Elsewhere in the San Joaquin Valley, the Etchegoin Formation has been the injection zone in many Class II waste disposal projects beginning in 1939 in the Greeley field. According to records of the California Division of Oil and Gas (Publication No. PRO6), more than 430 million barrels (1.8×10^{10} gallons) of waste fluids from various oil fields have been injected into this and other formations in Kern County through 1983.

Lithology and Environment of Deposition of the Reservoir

The San Joaquin Formation is characterized by shallow marine fine-grained sands, silts, and clays. The Etchegoin Formation is characterized by massive blue and brown sandstones, poorly sorted shales and pebble conglomerates (Foss & Blaisdell, 1968).

The San Joaquin-Etchegoin clays that separate thick sands are extremely low in permeability. Completion of injection wells in different portions of the sand (which are stratigraphically separated by clays) will result in vertical segregation of fluids. Clays comprise about 45% of the gross interval so there will be no difficulty in separating sand sections vertically above and below continuous clays which are 10 feet or greater in thickness.

Beneath the site, the injection zone has over 1,200 feet of net permeable sand within a total interval of 2,200 feet (see electric log section in Figure 6). The sands are continuous across the site but completely pinchout several miles away.

Reservoir Properties

Figure 7 summarizes the reservoir parameters derived from the nearest wells in surrounding oil fields and used in designing this project. The reservoir parameters of the injection zone listed below will be measured through whole core analysis, sidewall core analysis and injectivity testing at the injection site during the drilling of the first well.

- Hydraulic Conductivity or Permeability

  In surrounding oil fields the permeability has been found to be in the 1,000 to 2,500 millidarcy range.

- Porosity and Effective Porosity

  The assumed porosity for all calculations such as volumetric invasion of waste and pressure response was chosen as 30%, representing a conservative value. An effective porosity of 32.6% has been calculated from electric logs and an acoustic log response in the Western Continental Operating Co., NGC-CMI-BLC exploration well in Section 5, T.27S., R.20E, M.D.B.&M. and from electric log response in the Texaco, USA-Occidental Land Co., NCT-1, located in Section 8, T.27S, R.20E, M.D.B.&M. about 1 mile east of the proposed site.

- Reservoir Pressure

  The assumption of hydrostatic pressure or approximately 1,308 psia was made in all calculations for injection pressures and capacities.

- Storage Coefficient

$$S = f(w)\ h\ (B + \frac{\alpha}{\emptyset})$$

S = storage coefficient

$\emptyset$ = porosity - 30%

f(w) = ρg = specific weight of water per unit area or hydrostatic pressure per foot of aquifer thickness .433 psi/ft

h = aquifer thickness, inches 1,000 ft x 12"/ft = 12,000"

B = compressiblilty of water, square inches per pound

$$= 3 \times 10^{-6}\ \frac{in^2}{lb}$$

α = compressibility of aquifer skeleton square inches per pound

$$1 \times 10^{-4}\ \frac{in^2}{lb} \quad \text{[from Hall, 1953]}$$

$$S = .433\ lbs/in^2/ft\ (.3)\ (12000\ in.)\ \frac{(3 \times 10^{-6}\ \frac{in^2}{lb} + 1 \times 10^{-4}\ \frac{in^2}{lb})}{.3}$$

$$S = .1605564\ \frac{in}{ft} = 1.33797 \times 10^{-2}\ \frac{in}{in}$$

- Water/Oil Saturations

  In the area of injection, the San Joaquin-Etchegoin Formations are devoid of commercial hydrocarbon saturation as evidenced by extensive unsuccessful drilling.

  The San Joaquin-Etchegoin at the site and surrounding area is saturated with saline water. Salinity profiles show that within the injection zone the sands have calculated salinities significantly greater than 10,000 ppm. The total dissolved solids (TDS), calculated from electric logs, in general, range from 12,000 to more than 55,000 ppm in well OLC-NCT-1, No. 1 and 10,500 to 75,000 ppm in well NGC-CMI-BLC. Clearly, this zone does not provide a potential underground source for drinking water.

- Compressibility

  It is estimated that the compressibility of the aquifer skeleton is of the order of 1×10^{-4} in.^{2}/lb.

<u>Adequate Confinement Above and Below the Targeted Reservoir</u>

Lower Confining Zone

The Monterey Formation underlies the injection zone and is an ubiquitous shale regionally in the the Great Valley. For the most part, it is a deep marine shale and is frequently siliceous.

The following reservoir parameters of the lower confining zones would be measured at the injection site during the drilling of the first well.

- Hydraulic Conductivity or Permeability

  The hydraulic conductivity or permeability of the lower confining zone is negligible. It is an impermeable zone due to its high shale and low sand content.

- Porosity

  The porosity of the Monterey Formation has been measured between 35% and 70%, however, the individual pore spaces are not interconnected so permeability is negligible.

- Oil/Water Saturation

  Oil saturation in the Monterey Formation in the confining zone at the site is negligible. The confining zone is estimated to be saturated with connate water of salinities over 10,000 ppm.

- Compressibility

  The compressibility of the Monterey Formation confining zone has not been tested in the area of interest.

Lithology and Environment of Deposition of Upper Confining Zone

The Tulare Formation of Pleistocene age is approximately 1,900 feet thick in the project area. The lower 400 feet of this formation is dominately tight shale and provides the upper confining layer over the San Joaquin-Etchegoin injection zone.

The Tulare Formation is primarily composed of silicate detritus. Woodring, et al, 1940, established that the Tulare is nonmarine in origin. Figure 8, modified from Lennon, R.B., (1976 Fig. 1), is a map of the different Tulare environments based on paleontological and electric-log studies. East of the alluvial plain and shoreline environments in this part of the valley, the Tulare deposits beneath the site were accumulated in a lake environment in which shales composed of clays and silts dominated. This type of a lacustrine environment with a constant sediment influx precludes any possibility of limestone being deposited.

Petrophysical Properties

The following petrophysical parameters of the confining zone would be measured at the injection site during the drilling of the first monitoring well.

- Hydraulic Conductivity or Permeability

  The hydraulic conductivity or permeability of the confining zone is assumed to be negligible. It is an impermeable zone due to its high shale, low sand content.

- Porosity

  Due to the lack of permeability, the porosity of the Tulare shale has not frequently been measured in oilfield operations. According to Core Laboratories, Inc., the porosity typically will run 36-42 percent. This porosity is not effective or useable. It is total pore space. Total porosity is the ratio of the total void space in the rock to the bulk volume of the rock: effective porosity is the ratio of the interconnected void space in the rock to the bulk volume of the rock, each expressed in percent.

- Oil/Water Saturation

  Although the sandy portions of the Tulare Formation are productive of oil and gas in many fields in the general area, the oil saturation in the basal Tulare shale in the confined zone at the site is negligible. The confining zone is saturated with connate water of salinities in the range of 4,000 to 10,000 ppm.

- Compressibility

  The compressibility of the confining zone in basal Tulare shale would be tested when the first well is drilled. The Upper and Lower confining layers will provide significantly more than adequate protection from any upward or downward migration of injected fluids at the site.

<u>Detailed Hydrogeologic Understanding of the Chosen Site</u>

The sediments above the upper confining layer are collectively considered the groundwater aquifer for the purposes of this report. As discussed below, the interval delineated as a fresh water aquifer not only contains water of inferior quality (4,000-10,000 ppm TDS), but the lithology expressed by logs from nearby abandoned exploratory oil wells, (90-100% shale), suggests the lack of an available recharge system.

Lithology of Aquifer

Subsurface mapping suggests that the lithologic description of the aquifer can be divided into two distinct units: a) the upper 300-400 feet of the alluvium deposits and b) the remaining lacustrine Tulare deposits.

As previously discussed, the Tulare Formation in the vicinity of the site was deposited as a lacustrine shale (Figure 8). At the site, the remaining Tulare Formation above the confining layer is probably 100% shale.

The alluvium is composed of poorly-sorted unconsolidated sands with minor thin interbedded shales. The upper sands are usually moisture deficient, (i.e., air-filled porosity) throughout the region. No perched water has been identified by the wells that have been drilled in the area.

Only near the base of the alluvium do the lenticular sands interfinger with Tulare shales and form pockets of permeability to hold water. The source area for the alluvial and Tulare sediments is the Temblor Range to the west. The individual alluvial lentils are amalgamated sands for the most part, however, water is sometimes trapped in the basal alluvium deposits.

The occurrence of useable water has limited documentation. There are no active water wells in the basin. Regionally, Bliss (1972, p.7) described the area as follows:

> ".....the area is cursed with limited or nonexistent groundwater resources throughout most its extent. Soils are deep and apparently fertile, but severe salinity and boron problems occur in some places that appear otherwise promising for agriculture development."

Groundwater with quality suitable for irrigation appears to be restricted to the Kettleman Plain, McClure Valley, Devils Den area, and Antelope Valley. These areas were the only ones where irrigated agriculture had been active for several decades prior to the importation of surface supplies (Wood and Davis, 1959). East of the aqueduct, groundwater of good quality, originating from the Kern River, is extracted for general use at this time.

Surface Water

The area of interest is characterized at the surface by gently sloping alluvial fan deposits notable for small and flashy water discharge (Wood and Davis, 1959, p.49). The lack of good definition of any stream channels and the moisture deficient condition of the alluvial deposits are the result of surface runoff composed entirely of rare flood discharge that lasts for a few hours to a few days.

There are no gauging stations on the site but Wood and Davis (1959) concluded that the mean annual runoff is sparse. It is not considered a significant source of recharge to groundwater. Precipitation is less than 6 inches per year.

The nearest gauging station is located in Bitterwater Creek (7-1/2 miles west of site). A sample of surface runoff was collected and analyzed in 1952 (Wood and Davis 1959, Table 9). The chemical analysis from Bitterwater Creek sampled in Section 13, T.27S./R.20E., was analyzed with the following results: TDS = 3,200, Calcium = 500 ppm, Sodium = 320 ppm, Sulfates = 1,800 ppm, Chloride = 160 ppm, and Boron = 9 ppm.

Groundwater

No groundwater within the three mile radius of the proposed project site is currently being used for domestic supplies, irrigation or stock watering. During the early 1930's, however, a stock watering well was located near the north quarter corner of Section 9, T.27S./R.20E. A water quality sample from that well was analyzed on May 24, 1930, with the following results: Electrical Conductivity = 5,450 micromhos, TDS = 3,862 ppm, Calcium = 282 ppm, Sodium = 779 ppm, Sulfates = 1,775 ppm, Chlorides = 776 ppm, and Boron = 3.31 ppm (Rector 1983).

The level of free-standing historic groundwater is contoured in Figure 9. The surface corresponds to the approximate alluvium/Tulare boundary. This is not a coincidence: Tulare porosity is filled with connate water, the alluvial porosity is filled with air. The gradient of the groundwater movement from the site is to the northeast. In spite of the gradient contoured to the northeast, there is virtually no groundwater movement in the Tulare Shales.

No recharge is reflected in the map in the form of water level mounds and no withdrawal is occurring to otherwise modify the map. The apparent high to the southwest is a reflection of geologic structure. The connate water in the sands is essentially trapped.

The inability of the Tulare aquifer to yield water on a pump test also illustrates the limited extent of the sand bodies and generally the low permeability of the rocks. The Berrenda Mesa well, Sec. 28, T.26S./R.19E., drilled and abandoned in 1977, pumped 500 gal/min but with 221 feet drawdown after 24 hours. The Berrenda Mesa well, located 7-1/2 miles northwest of the site, is closer to the western source for Tulare sediments, and therefore sandier than what is anticipated at the site.

The chemical analyses of water from abandoned water wells from the Department of Water Resources and Wood and Davis (1959, Table 8) indicate an average TDS for the uppermost Tulare and alluvium of about 3,000-10,000 ppm.

The paleogeographic setting of the Tulare Formation (Figure 8), indicates that the fresh water aquifer, east of Lost Hills in the central and eastern portions of the Great Valley, cannot be contiguous with the Tulare Formation beneath the site. First, the sediment source area in the west is derived from outcropping older marine deposits. Second, the lacustrine portion has such low permeability that no recharge is diluting the connate saline condition except in a limited way in localized areas.

As an added measure, the Lost Hills anticlinal structure presents a significant barrier to connate water movement through the silty, clayey facies of the Tulare Formation. The presence of the largest known gypsite deposits in California on the west flanks of Lost Hills, lying between the site and the central portions of the Great Valley, indicates the barrier may have caused groundwater to rise to or nearly to the land surface (Wood and Davis 1959). These deposits are believed to be sedimentary in nature and related to Quaternary-aged floods from the Temblor Range that became temporarily ponded against the topographic barrier of Lost Hills.

Reasonable Seismic Stability

To avoid the destructive effects of an earthquake, planners need to know the location of active faults and the relative seismic activity in the vicinity of the site (Ziony and Yerkes, 1985). With regard to this project, those subjects were considered and indicate the disposal site is a relatively stable location.

The tectonic forces that have shaped the geology of Western United States are still active. Tectonic uplift of the Coast Ranges, punctuated by earthquakes due to displacement along various fault zones, has occurred in historical time. The recent Coalinga earthquake, as well as several documented earthquakes along the well-known San Andreas Fault zone, indicate that various seismic sources are active within the region.

The contour map of epicenter density per township in Kern County (Figure 10) illustrates that no earthquake epicenters have been recorded in the immediate project area. The site is an area of extremely low epicenter density. Elsewhere, earthquakes of a magnitude less than 4.0 on the Richter Scale are a common occurrence in California. One such earthquake was recorded approximately 1.5 miles to the southeast of the project site. The California Division of Mines and Geology does not record earthquakes of a magnitude less than 4.0 on the Richter Scale since they pose no significant geologic hazard. Furthermore, the project site is not located within an Alquist-Priolo Special Studies Zone.

The nearest known active fault to the project site is the San Andreas Fault, (refer to Figure 3), located approximately 13 miles west. All of the associated epicenters fall outside of Kern County and therefore are not reflected in Figure 10. Recent trenching studies (Sieh and Jahns, 1984) indicate that a maximum magnitude earthquake of 8.0 could occur on this section of the San Andreas Fault in an interval of approximately 240 to 450 years. Based on the distance from the fault to the proposed project site and the soil profile of the site, an earthquake with this magnitude could produce horizontal ground accelerations at the site in the range of 0.3 to 0.35 g.

The most recent earthquake of magnitude 8 on the segment of the San Andreas Fault near the project site occurred in 1857. That earthquake did not produce any secondary faulting at the project site. Considering the short recurrence intervals for large magnitude earthquakes on the San Andreas Fault, there have been numerous opportunities for secondary faulting to have occurred at the site during the Holocene (last 10,000 years); however, no faulting has been observed. Based on these observations and the site geology, it is concluded that future tectonic activity in the vicinity of the site, if it were to occur, most likely will further modify existing fold sets rather than create new faults.

Induced Seismicity

As previously mentioned, most of the oil and gas fields in western Kern County inject large volumes of fluids with no known seismic effects. Much of this injection is into the same San Joaquin-Etchegoin Formations targeted as the reservoir for the proposed project. No earthquakes have been reported relating to these oil field injections. The proposed project would add approximately 1.6 percent to the total amount injected for all oil field operations annually in Kern County. Over the project life, this amount would be less than 1 percent of the total cumulative injection in Kern County.

Compatability Between Liquid Waste Material, Reservoir Fluids and Matrix, and Materials of Construction

Many problems due to compatibility may be encountered in a commercial hazardous waste injection project. As discussed by Hower et al, 1972, the following methodology has been utilized to determine the total feasibility of the project.

- The geology of the area has been thoroughly defined.
- The drilling and completion program of the wells has been designed to obtain the maximum usable data and to resist a wide variety of chemical substances.
- The injection zone will be properly isolated mechanically and geologically.
- Realistic laboratory tests have been designed to thoroughly analyze the rock matrix and determine rock and native reservoir fluid compatibility with the intended injectate and to define pretreatment requirements.
- All wastes received at the facility will be determined to be compatible before acceptance.
- An extensive monitoring system for reservoir damage or construction material damage has been designed.

Hydrologic Effects of Injection in the Reservoir

The hydrologic effects of injection on the reservoir can be considered threefold; 1) pressure buildup, 2) invasion radius or affected area, and 3) injection zone and upper confining layer communication or pollution potential.

Pressure Buildup

The pressure buildup for the San Joaquin-Etchegoin was evaluated considering the geologic picture of the particular site. Several equations, all related, are commonly utilized to estimate the increase in pressure. They are the Bernard Formula, the Theis Equation, and the Diffusivity Equation. All yield satisfactory results with the proper application of the limiting parameters. The limiting parameters for the site were unconsolidated sands, no injection or production from the same sands, individual sand mapping and volumetrics and a fluid-filled matrix. The pressure increases over the lifetime of the Rhetta project were calculated to be of the order of fifty psia, which is far less than what would be required to fracture the formation.

Invasion Radius

A good estimate of the minimum distance of wastewater flow from an injection well can be made by assuming that the wastewater will uniformly occupy an expanding cylinder with the well or wells at the center. The equation for this case is:

$$r = \left(\frac{V}{b\,\emptyset} \right)^{\frac{1}{2}}$$

where r = radial distance of wastewater front from the well

V = cumulative volume of injected wastewater

b = effective reservoir thickness

$\emptyset$ = average effective porosity

The results of this calculation are shown in graphic presentation in Figure 11.

As discussed by Warner and Lehr (1977), the minimum distance of travel will be exceeded due to dispersion, density segregation, and channeling through high permeability zones. An estimate of the influence of dispersion can be made with the following equation:

$$r^{1} = r + 2.3\ (Dr)^{\frac{1}{2}} \quad \text{(Bear, 1972)}$$

where r^{1} = radial distance to travel with dispersion

r = 100% invasion radius from previous calculation

D = dispersion coefficient; 3 feet for sandstone aquifers (Bear, 1972)

The dispersed radius has been calculated and the results are shown graphically in Figure 11.

Although the projected effecitve thickness of the injection zone is 1,200 feet, the preceeding calculations were submitted with an individual well thickness of 300 feet. The completions of the individual wells will be stratigraphically separated to eliminate or minimize mixing of injectate over the life of the project.

The dispersion radius has been plotted on Figure 12 around each of the proposed injection wells and defines the area of influence of the injected wastewater.

Injection Zone and Upper Confining Layer Communication

Injection zone and upper confining layer communications is defined by the geology and the pressure increases induced by injection. The confining layer must be a real and demonstratable barrier to fluid migration. The thick incompetent shale member of the Tulare is such a barrier. The effectiveness of the barrier can be demonstrated in several ways. First, the same basal Tulare shale confines gas and oil within six miles. Secondly, there is a definite salinity profile breakover in the stratigraphic column. Thirdly, a forty day "leaky" aquifer test has been designed which will clearly demonstrate potential leakage during the pre-injection testing phase of the well construction procedure.

CONCLUSIONS

Proper evaluation for proposed hazardous waste injection sites can be done in such a manner that protection of drinking water sources and other resources is ensured. The combined efforts of the different scientific disciplines brought together by Evans, Carey and Crozier in the study of the proposed Rhetta Facility site has resulted in locating and describing the site which is probably as close to ideal as will be found in California.

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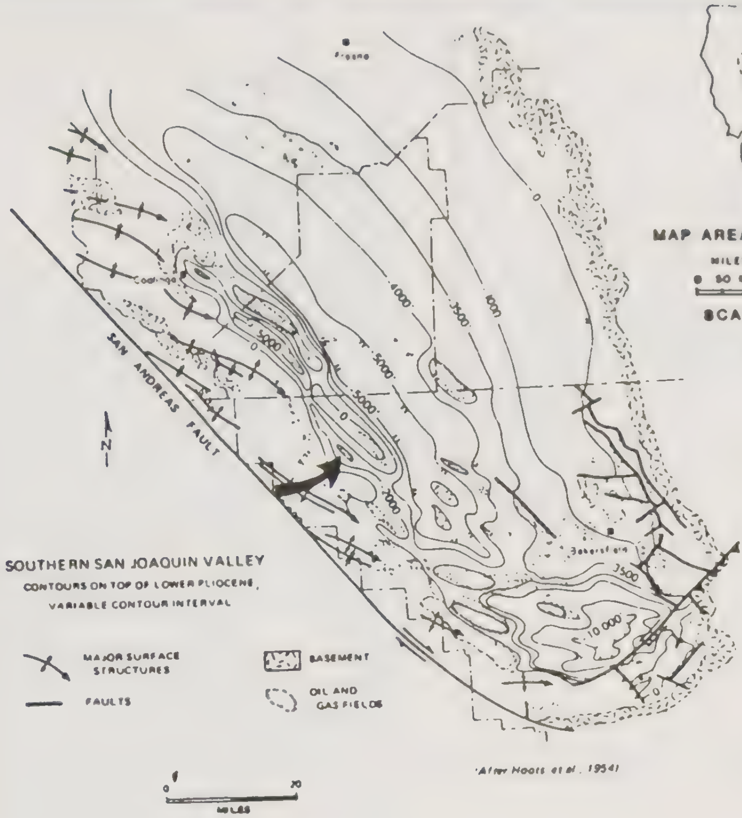
Figure 1.
Location of California's Class I Hazardous Waste Disposal Facilities.

Figure 2.
Potentially Suitable Basins in Deep Waste-Injection Well-Site Evaluation (Adapted from Warner and Lehr, 1977). Arrow points to proposed site.



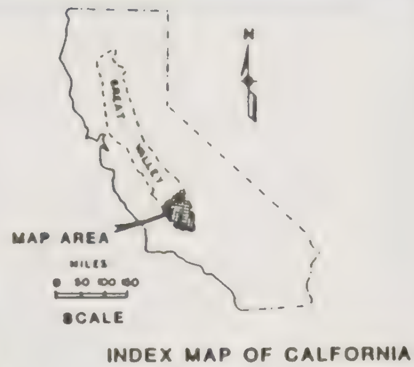


Figure 3.
San Andreas fault, surface fold axes in adjacent Diablo and Temblor Ranges, subsurface structure contours, and oil and gas fields of San Joaquin Valley basin. (from Harding 1976, figure 1).

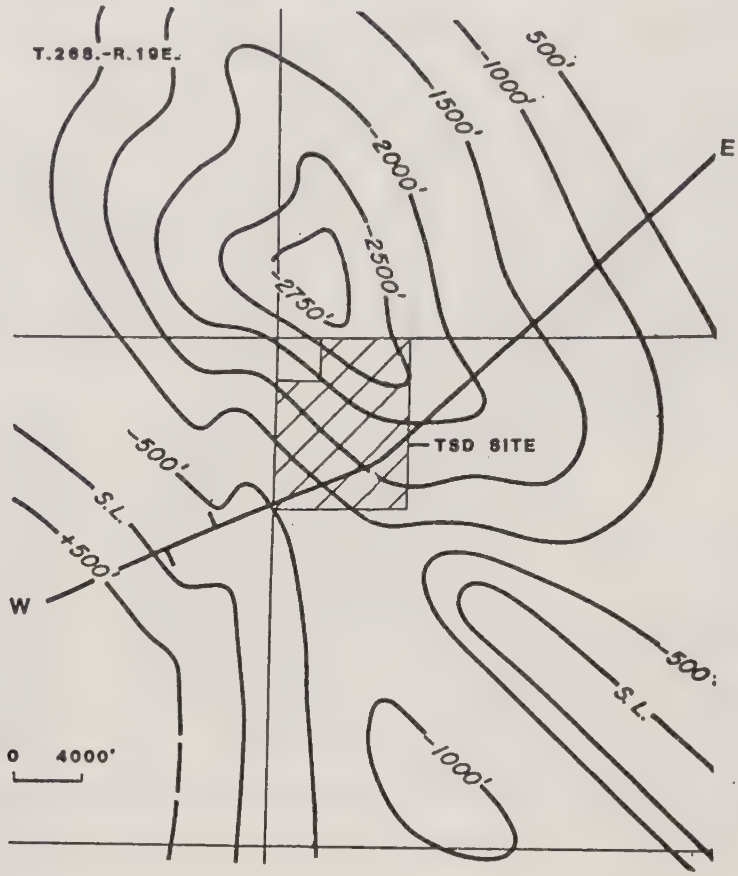


Figure 4.
Structure Contours on top Injection Zone, San Joaquin–Etchegoin Formation.

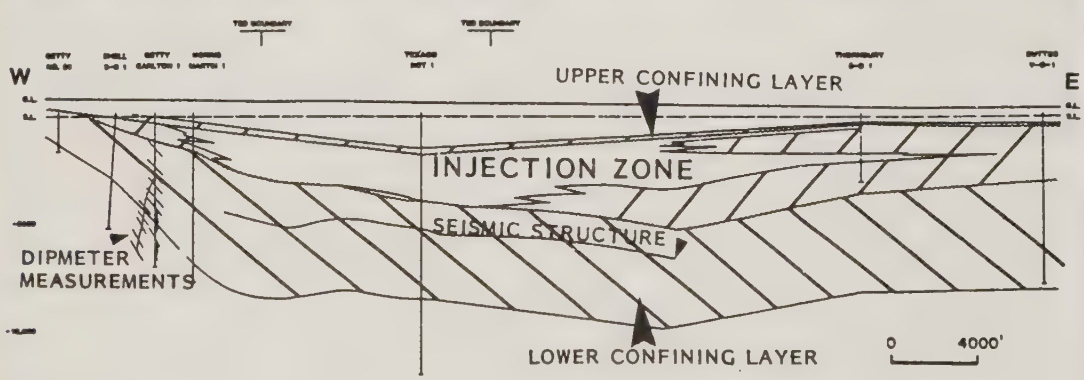


Figure 5.
Southwest-Northeast Cross Section through proposed disposal site. See Figure 4 for location.

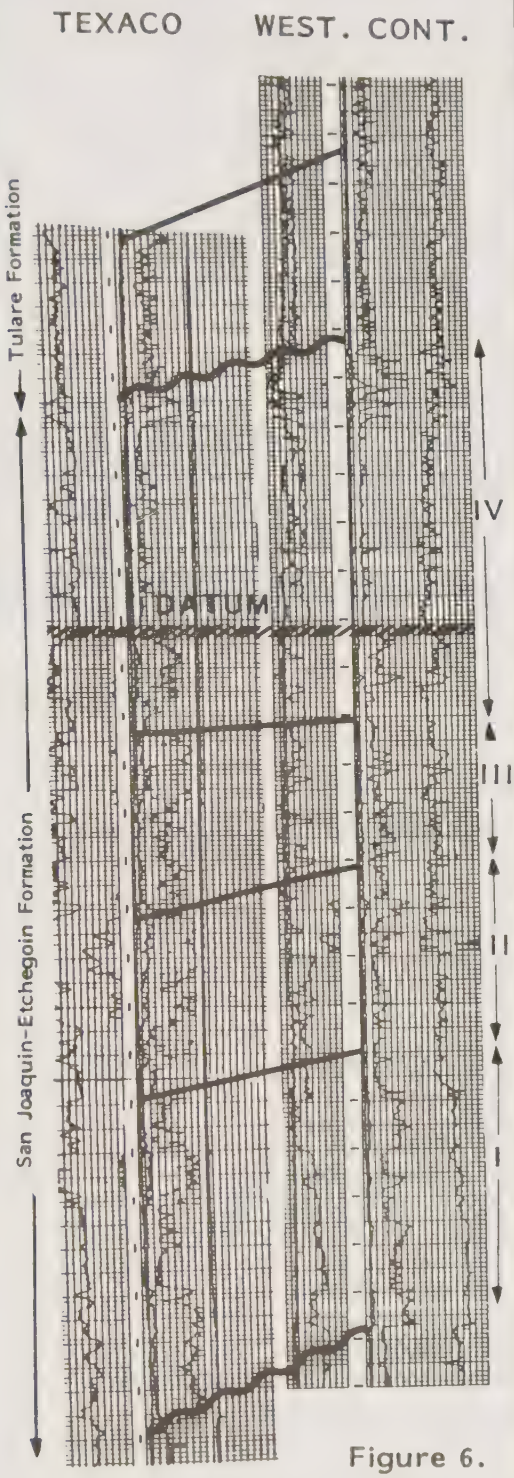


Figure 6.

Stratigraphic Section depicting electric log response in injection zone. Isopach interval groups identified on right as I-IV.

Top of Injection Zone, Elevation, feet	1900
Bottom of Injection Zone, Drilled Depth, feet	4140
Bottom Hole Pressure Gradient, psi/ft	.433
Average Injection Rate, per well, gpm (steady-state flow rate)	300
Volume of Injected Fluid, 4 wells, gpd	1.7×10^6
Temperature Gradient °F/100 ft +70°	1.0
Anticipated Reservoir Pressure, psi	1308
Viscosity of Injection Fluid, centipoise	1.0@ 60°F
Anticipated Reservoir Temperature °F	125
Temperature of Injection Fluid °F	80
Porosity, percentage	32.6%
Permeability, millidarcies	1000-2500
Rock Compressibility psi^{-1}	3.5×10^{-6}
Fracture Gradient* psi/ft	.80
Net Formation Thickness, feet	1200

*Fracture gradient will be further quantified with injectivity of the first well drilled by TSD. The Division of Oil and Gas of the State of California recommended the use of .8 psi/ft fracture gradient until the injectivity test could be accomplished.

Figure 7.
Summary of Injection Zone Data.

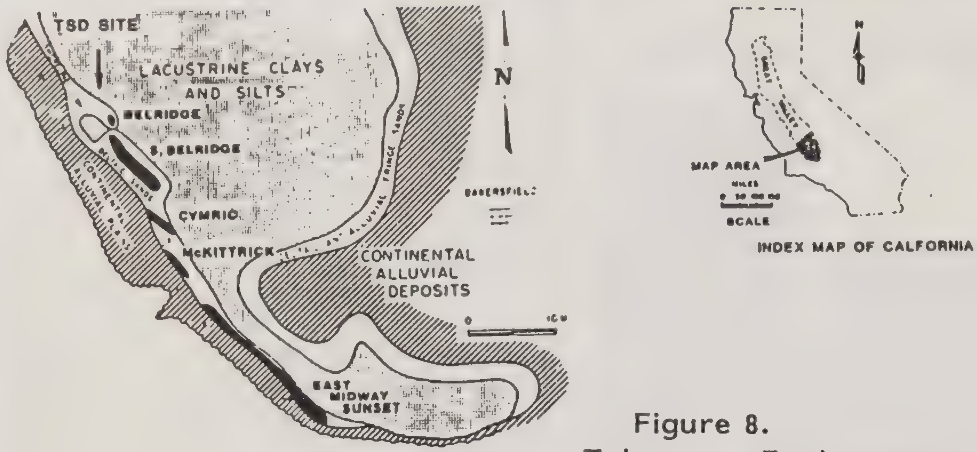


Figure 8.
Tulare Environments of depostion in the Southern San Joaquin basin, California (Lennon, 1976, Figure 1).

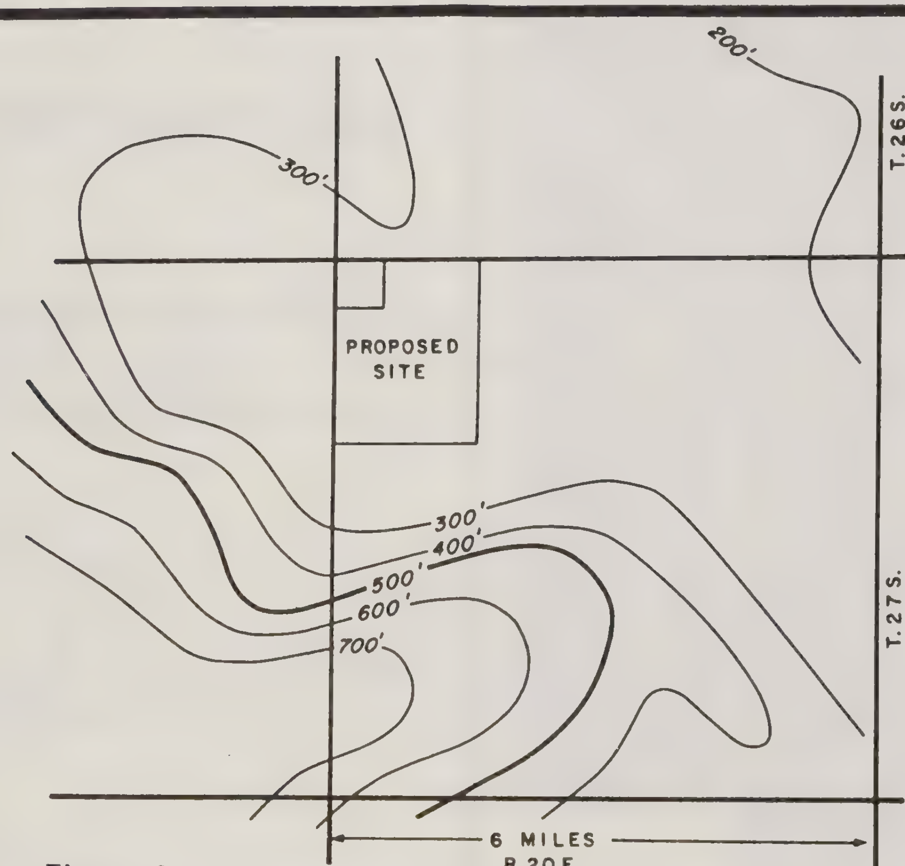


Figure 9.
Groundwater Elevation Map (Contour depth represent distance above sea level datum).

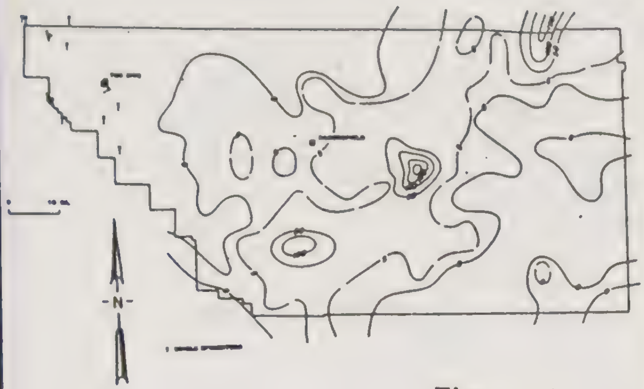


Figure 10.

Kern County Epicenter Density Per Township, 1932-1985 (Kern County Seismic Hazard Atlas prepared by Kern County Planning Dept. updated by ECC, 1985).

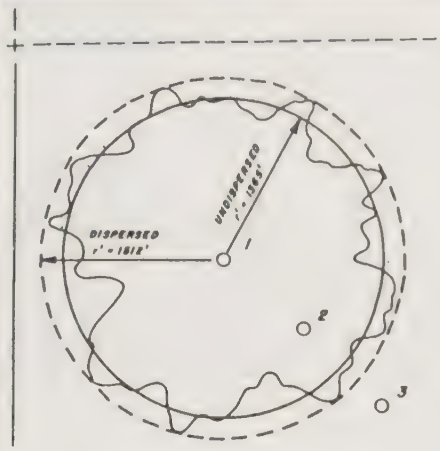


Figure 11.
Dispersed and Undispersed Injectate Fronts.

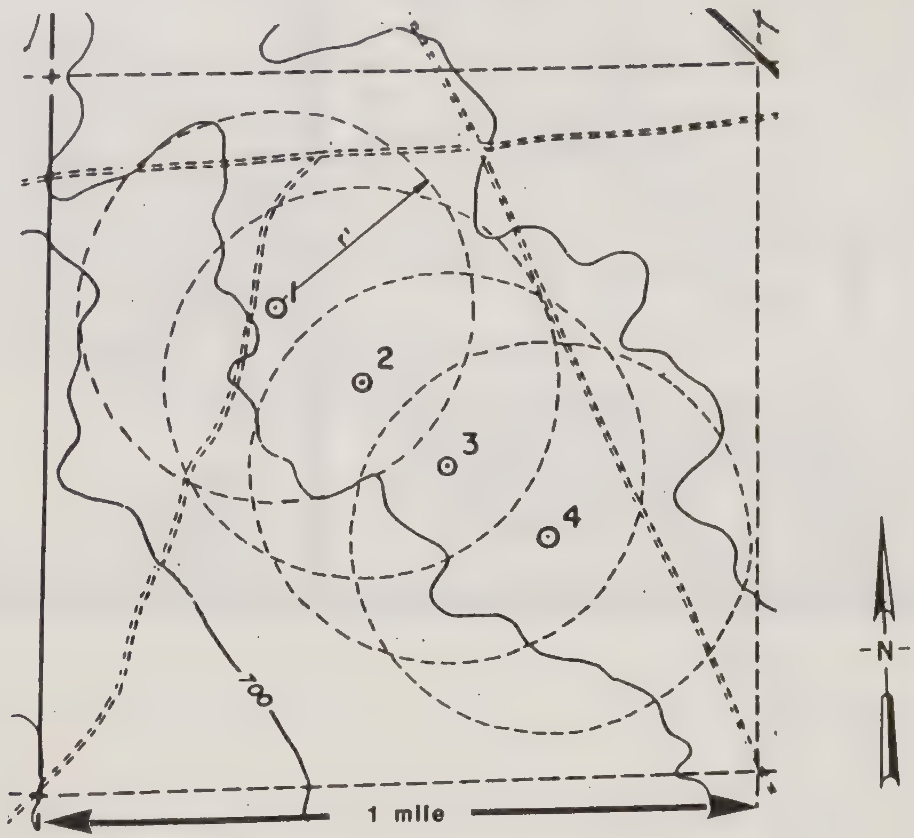


Figure 12. Area of Influence Dispersion Radius.

EXHAUST GAS SCRUBBING
FOR SEMICONDUCTOR PROCESSES

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Abstract

In the present paper we describe a scrubbing system, which removes the toxic compounds from the exhaust gases of silicon as well as III-V semiconductor equipments. The principle of the cleansing process is based on the reaction of covalent hydrides like arsine and phosphine with iodic acid solution to the corresponding acids. Metal-organic as well as group-V-compounds, which are also contained in the exhaust gas of vapor phase epitaxy (VPE) reactors form water soluble salts and acids. These reactions are carried out in an absorption column. The developed scrubbing system is capable to remove hydrides to concentrations below 1 ppb (detection limit).

1. Introduction

The fabrication of electronic and optoelectronic devices on III-V /1/ and Silicon semiconductor layer systems requires several vapor phase epitaxial and etching techniques using toxic, dangerous and odor troubling gases. The handling, use and disposal of those gases and vapors present a formidable safety task where three subjects have received a great deal of recent attention: worker safety, atmospheric and water pollution.

Due to the raising restrictions on process gas emissions caused by the mentioned subjects and the lack of efficiency of methods like activated-charcoal beds or thermal decomposition wet chemical scrubbing systems have to fulfill the demand for efficient gas cleansing. Since also water pollution is another problem not only in the field of semiconductor industry this paper will report the development of a patened /2/, efficient, closed wet chemical scrubbing process /3/.

2. Semiconductor processes and their employed gases

The semiconductor industry includes many sources of air pollution. Of immediate concern is silicon wafer processing, in which preparation and wet etching generate hydrocarbon and acid vapor in

high concentrations, which are usally handled by central (plant) adsorption devices and scrubbers.

The newer and fast raising wafer processing techniques such as epitaxial deposition (Metalorganic VPE, Halide VPE), plasma etching and ion implantation introduce many gases that are extremely toxic, carcinogenic or combustible. Although the processes consume only small quantities of those gases, they require special attention due to the nature of both reactant and product gases. The nature of the gases is such that already small amounts of gas can do considerable damage to people and equipment in a very short time. While the safe handling of the reactant gases is up to the design and the security equipment of the semiconductor machines, the exhaust gases have to be decontaminated by an additional efficient cleansing system.

The composition of the exhaust gas depends on the specific process as mentioned above and on the materials to be grown. In the MOVPE and the hydride VPE of III-V compounds /4,5/ the toxic covalent hydrides of the pnictides as arsine, phosphine and stibine are used to provide the group-V-elements and silane, hydrogen sulfide, selenide and telluride for doping. Furthermore in the halide VPE hydrogen chloride is used as an essential process gas. Metalorganic compounds of the group-III-elements are used in the MOVPE process, e. g. the alkyls of gallium, indium, aluminum, tin or zinc. Table 1 gives details of some of the hazards of the gases used in semiconductor industry. To give a scale for their hazard the maximum allowable working place concentration (MAK, correponding to TWA in the USA), as it is fixed in West Germany is listed in one column.

Table 1: Gases commonly used in semiconductor industry /6,7/

	Formula	MAK ppm	Hazard
Ammonia	NH_3	50	toxic, flammable
Arsine	AsH_3	0.05	extremely toxic, flammable
Phosphine	PH_3	0.1	extremely toxic, pyrophoric, flammable
Hydrogen chloride	HCl	5	corrosiv, toxic
Hydrogen sulfide	H_2S	10	toxic, flammable
Chlorine	Cl_2	0.5	corrosive, toxic
Silane	SiH_4	0.5	flammable, pyrophoric, toxic
Diborane	B_2H_6	0.1	extremely toxic, flammable
Hydrogen selenide	H_2Se	0.05	extremely toxic, flammable
Hydrogen telluride	H_2Te	-	unknown
Alkyl-gallium	R_3Ga	-	flammable
Alkyl-indium	R_3In	-	unknown
Alkyl-aluminum	R_3Al	-	pyrophoric
Alkyl-tin	R_3Sn	-	unknown
Alkyl-zinc	R_3Zn	-	toxic, flammable
Alkyl-magnesium	R_3Mg	-	unknown
Alkyl-arsenic	R_3As	-	extremely toxic
Alkyl-phosphorous	R_3P	-	toxic, pyrophoric

3. Methods of decontamination

In most cases still the following methods are in application to decontaminate the exhaust gases from semiconductor reactors /8/:

(i) Diluting by air to a none toxic concentration and ventilation into the atmosphere
(ii) Physical adsorption (e. g. activated-charcoal filters)
(iii) Burning in hydrogen-oxygen flames and desorption of the resulting oxides in water to form the corresponding acids
(iv) Pyrolyzation at high temperatures

The first "process" should be replaced by an efficient decomposition process, because even smallest amounts of the mentioned gases are extremely toxic and any contamination is to avoid.

The adsorption of the gases with activated-charcoal beds, where the primary removal mechanism is surface retention has several disadvantages: large amounts of adsorption materials are required, the charcoal has to be prepared differently for different compounds and the soiled charcoal still has to be disponed properly

Burning the gases in hydrogen-oxygen flames includes the danger of explosion, because many of the contaminants are combustible themselves. Thus extreme care is necessary in the areas of safety and control of byproduct emission, which again can be corrosive, toxic and odorous as well.

Pyrolyzation even at high temperatures is in some cases not efficient enough to completely crack of the dangerous compounds.

Since now the method of wet chemical scrubbing and dissolution in water is left unmentioned. Compared to the proceedures described above only this method provides a safe and efficient way to remove the toxic, corrosive or odorous compounds from the exhaust of semiconductor processes. Those chemical scrubbing systems are constructed on the basis of either spray and baffle chambers or packed-bed counterflow columns followed by particle filters. In order to obtain the most effective decontamination the critical parameters as gas velocity, free cross section of the column, surface area available for the reaction /9/ as well as the most important point, the reaction chemicals themselves have to be chosen well. Since water pollution has to be avoided closed recirculation systems with highly concentrated chemicals are most advantageous. Various aqueous solutions of potassium permanganate, sodium hydroxide, cupper sulfate or sodium hypochlorite have been employed /10/. But an efficient decontamination - below 100 ppb - of all semiconductor gases with one of the solutions could not be reached.

In the present work we introduce a novel method, which relies on directly oxidation of the toxic compounds in the liquid phase without previous burning as needed in some of the processes reported above. The developed method proves to be highly suitable for MOVPE, halide VPE as well as for silicon semiconductor processes. A manufactured scrubber will be described.

4. Chemical decontamination reactions

In chemical literature only a few studies have been published, which refer to oxidation reactions of the mentioned compounds of the exhaust semiconductor gases. Moser et al. /11/ reported that iodic acid reacts immediatly with phosphine under formation of phosphoric acid according to following equation.

$$8\ HJO_3 + 5\ PH_3 \leftrightarrow 5\ H_3PO_4 + 4\ J_2 + 4\ H_2O \quad (1)$$

The authors exploited this reaction for the analytical detection of traces of phosphine in coal gas.

Similar analytical experiments were performed by Reckleben et al. /12/, who verified a corresponding reaction for arsine with iodic acid:

$$8\ HJO_3 + 5\ AsH_3 \leftrightarrow 5\ H_3AsO_4 + 4\ J_2 + 4\ H_2O \quad (2)$$

They also reported about the catalytical enhancement of the originating iodine.

For other covalent hydrides only the reaction of hydrogen sulfide with iodic acid has been reported /13/.

For exotic metalorganic compounds used in MOVPE processes to our knowledge no oxidation reactions have been reported. However, in the experimental organic chemistry it is well known that such compounds can be decomposed by alcoholic iodine solutions. Our experiments disclosed that e. g. trialkyl phosphines, which appear to be unsoluble in water, can be converted into phosphonium salts by reactions with acids. These compounds are water soluble and can be oxidized by iodic acid.

5. Experiments

To assess the oxidation efficiency of iodic acid, preliminary tests were carried out for arsine, phosphine and trimethyl phosphine respectively using an experimental set up as drawn in fig. 1. Three flasks coupled in series were connected to the respective gas supply channels: the bubbler in the middle was filled with iodic acid (100 ml), whereas the first flaskbottle served to prevent the back-flow of the reaction solution into the gas tubes. During bubbling the gases to be tested through the iodic acid solution, iodine vapor was released, which was found to interfere with the measurements of the residual gas concentrations. For this purpose a commercially available monitor (L`air liquide company) connected to the outlet was employed, which detects the chemoluminiscence radiation generated by a hydride-ozone reaction. The iodine vapor tends to disturb this reaction. Consequently, a third bottle was attached, which contained a solution of potassium hydroxide to react with the iodine vapor to form potassium iodid and potassium iodate by disproportionation according to:

$$3\ J_2 + 6\ KOH \leftrightarrow KJO_3 + 5\ KJ + 3\ H_2O \quad (3)$$

It should be pointed out here that the potassium hydroxide solution has the additional function of removing hydrogen chloride and other halogenides from the exhaust gas by neutralisation and Chlorine by disproportionation.

As test conditions a hydrogen carrier flow of 5 l/min was chosen and the concentration of arsine and phosphine respectively was increased up to 2500 ppm. For this maximum value a remaining concentration at the outlet of less than 2 ppm was determined (detection limit 1 ppb). In case of trimethyl phosphine the maximum input concentration was adjusted to 380 ppm. Unfortunately the used monitor was not calibrated for this gas. However it appears reasonable to assume a value roughly equivalent to that of arsine and phosphine. On this assumption an outlet concentration of around 1 ppm was measured /14/.

These results imply that the oxidation of hydrides and also alkyl phosphines by iodic acid can be exploited for a very efficient process to decontaminate the VPE exhaust gases. A considerable improvement of efficiency can evidently be attained by using larger reaction volumes.

Besides iodic acid also the less expensive alkali salts of this acid can be employed as suitable oxidizing agents. The reaction of these salts with the group-V-hydrides is as fast aş with the free acid provided the salt solutions are acidified. Howevěr the iodine salts exhibit considerable lower solubilities meaning that correspondingly larger solution volumes have to be used in order to achieve equivalent decontamination capacity /15/.

6. Design of the scrubbing system

On the basis of the results of the above investigations a two stage scrubbing system has been constructed (see fig. 2). Each stage consists of a counterflow column filled with ceramic Raschig rings, in which the chemical liquid is sprayed. Tanks for the liquids are installed under each column. After each stage demisters separate microdrops from the gas. At the outlet of the second stage the gas is cooled and the moisture in the gas phase is condensed. The condensate (pure water) which is led back into the first stage to refill evoporated liquid. An activated-charcoal filter serves as a safety trap at the exhaust. All containers, tubes, valves and the chemical pumps are made from Polypropylene. The circulation of the chemicals and the gas cooling are continously monitored by an electronic control unit. The system can be connected to several exhaust gas source lines.

The cleansing reaction mainly takes place in the columns, where the Raschig rings increase the surface for the reaction. Since in most VPE reactors the gas throughput is below 20 l/min, the standard columns are tailored that way that the gas velocity is always below 2 m/min.

At the end of the second stage before the gas has passed the activated-charcoal filter the residual arsine and phosphine concentrations have been measured, while at the gas inlet a constant flow of 20 l/min hydrogen with 1 % of the hydride was maintained. A conventional gas monitor has been used with a detection limit for arsine and phos-

phine of 1 and 2 ppb respectively. Even at this high input concentrations no detection was notified. For long term use the capacity of the container contents allows the use of one chemical charge to decontaminate more than 1,000 l of the hydrides.

7. Summary

We have developed a scrubbing process for the exhaust gases of VPE systems as used in the III-V technology. The content of covalent hydrides like arsine and phosphine has been reduced below 1 ppb. In addition trialkyl phosphine vicarious for most of the group-V-alkyls and metalorganic compounds used in the VPE can also be oxidized. A constructed scrubber system has been operated continously since almost three years without problems. It should be noted that also other hydrides like silane, hydrogen sulfide and selenide as well as ammonia will react efficiently with iodic acid. Therefore the described system should be useable in the silicon and the II-VI technology. On reactions of iodic acid with heterocyclic thio and seleno compounds, which can also be used as sources for the latter material systems, no experiments are known to date /16, 17/. However, provided a high enough basicity of these compounds an efficient oxidation by iodine contained in iodic acid solutions can be expected.

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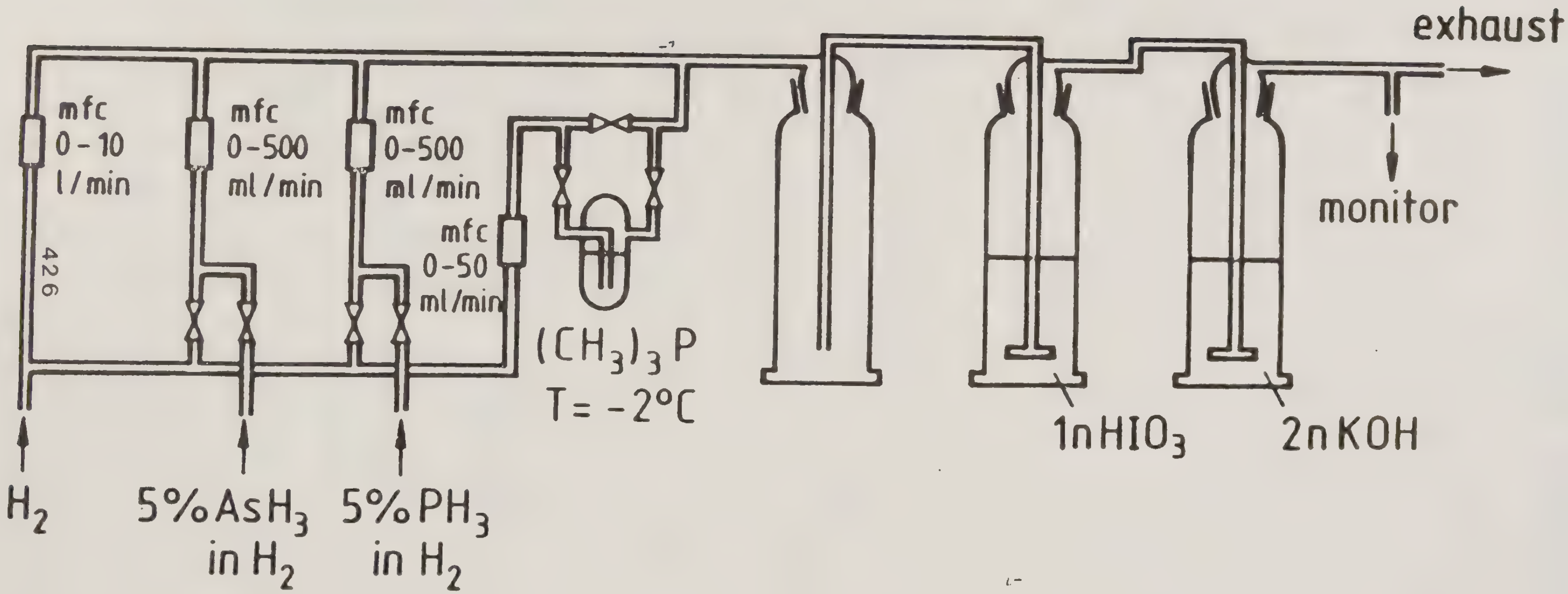
figure captions:

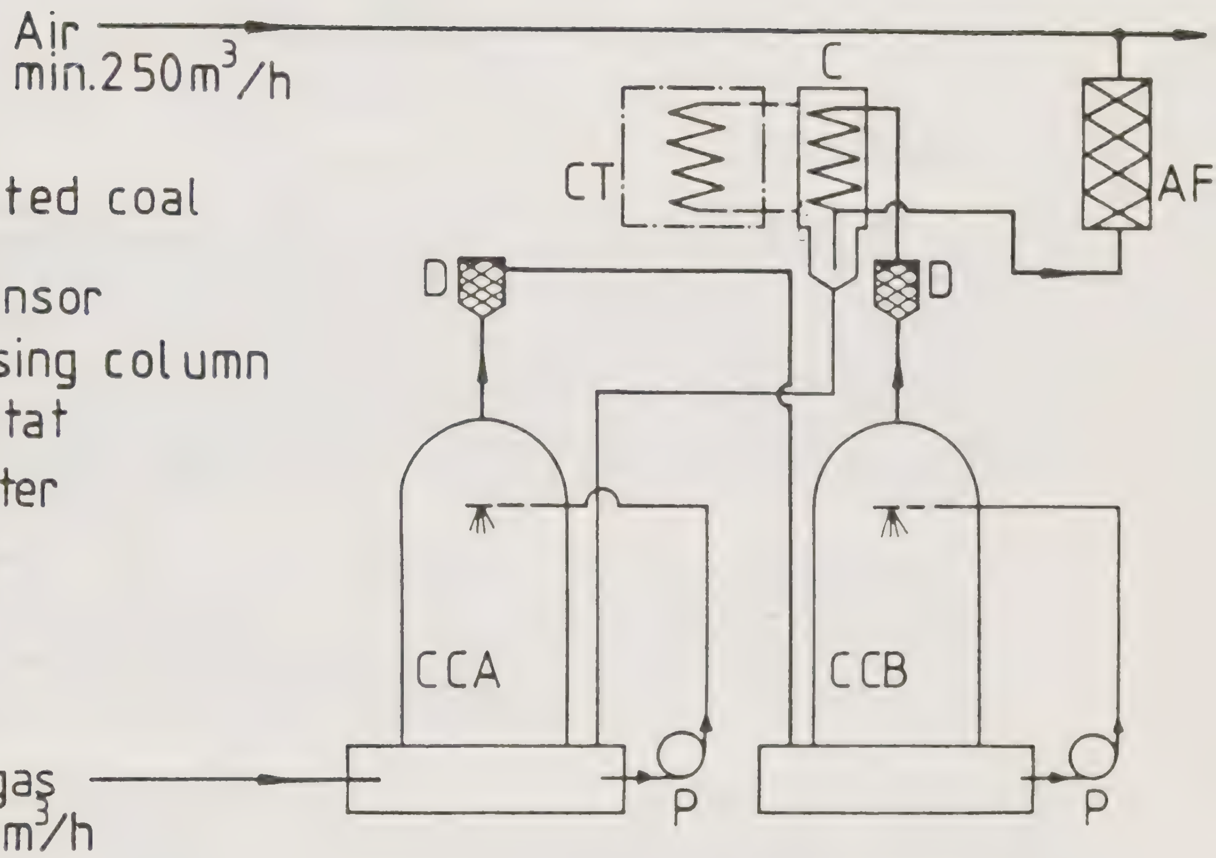
fig. 1: Experimental set-up for investigation of the reaction efficiency of iodic acid for arsine, phosphine and trimethyl gallium.

fig. 2: Schematic diagram of the scrubbing system.



exhaust
mfc
0 - 10
l/min
mfc
0-500
ml/min
mfc
0-500
ml/min
mfc
0-50
ml/min
(CH3)3 P
T= -2°C
monitor
1n HIO3
2n KOH
H2
5% AsH3
in H2
5% PH3
in H2

fig. 1



AF-activated coal filter
C - condensor
CC-cleansing column
CT-cryostat
D - demister
P - pump

fig. 2

GRANULAR ACTIVATED CARBON ADSORPTION WITH AIR STRIPPING FOR GROUNDWATER TREATMENT

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INTRODUCTION

The contamination of groundwater by organic chemicals has become a national concern, and steps have been taken by industry and government to cleanup sources of contamination and by potable water suppliers to treat water prior to distribution. In cleaning up contamination sources, industry and government have frequently found it necessary to intercept and treat groundwater that has already been contaminated. Concern over groundwater quality is well justified as nearly half of the population of the U.S. relies on groundwater as a source of drinking water, and estimates indicate that 15 to 20 percent of groundwater sources may already contain some level of organic chemical contamination.[1]

Predominant among such contamination is the presence of volatile organic contaminants (VOC's) such as chlorinated solvents and aromatics. The U.S. Environmental Protection Agency has recognized that some of these VOC's may have chronic toxicity and has proposed maximum contaminant levels (MCL's) for eight VOC's in drinking water with other compounds under study.[2] Some of the proposed limits are as follows:

Compound	Proposed MCL (mg/l)
Trichloroethylene	0.005
Carbon Tetrachloride	0.005
1,2-Dichloroethane	0.005
Benzene	0.005
1,1-Dichloroethylene	0.007

AIR STRIPPING TREATMENT

With the increasing discovery of VOC's in groundwaters and the acknowledgement of their potential health risks, considerable study and analysis has been done on methods to effect their removal from water. In

recent years, the aeration process has been given a great deal of attention in both studies and in actual applications. The aeration process depends upon the contaminant being more volatile relative to water so it can be removed from the water into the air. A measure of a contaminant's relative volatility is provided by its Henry's Law Constant, which is directly proportional to its vapor pressure and inversely proportional to its solubility in water. Some typical Henry's Law Constants at 20°C as measured by concentration in air relative to it's concentration in water (dimensionless) are as follows:

Compound	Henry's Law Constant[3]
1,1-Dichloroethylene	7.8
Carbon Tetrachloride	1.2
Tetrachloroethylene	1.1
Trichloroethylene	0.48
Benzene	0.22
1,2-Dichloroethane	0.05

The most effective application of the aeration process is through the use of packed tower air strippers. The design of the packed tower is based upon the number of "transfer units" in which the contaminant partitions itself between the air and water phases. The number of these transfer units is influenced by water and air rates, type of packing and the overall tower height. In general, a well designed packed tower air stripper can achieve approximately 99% removal of VOC's with Henry's Law Constants greater than 0.1. In pilot tests, we obtained the following removals of VOC's in the ppb range using a 10 ft. deep packed bed at a 50-1 air-water ratio.

Compound	Removal
Trichloroethylene	94%
Tetrachloroethylene	97%
1,1,1-Trichloroethane	94%
1,1-Dichloroethane	92%

Overall costs including the capital expense of constructing a FRP packed tower with plastic packing, and operating costs consisting of blower and pump motor electrical expense plus possible periodic cleaning of the media have indicated overall packed tower costs in the range of 8.2 to 29.6 cents per 1,000 gallons treated.[4]

Air stripping systems have two characteristics that require detailed evaluation on the part of the designer. One factor is that even 99% removal of contaminants may not suffice to meet the levels for drinking water standards noted above. Another factor is that the VOC's being discharged into the surrounding air are coming under greater scrutiny. The USEPA has already stated that it intends to name trichloroethylene and tetrachloroethylene as hazardous air pollutants[5], and some states

have required treatment of the air stripper off-gases to insure complete removal of the contaminants from the environment.

If either of these factors come into play, then air stripping will often have to be combined with other processes.

GRANULAR ACTIVATED CARBON TREATMENT

Adsorption with granular activated carbon (GAC) is a technology that has received widespread use in removing VOC's from groundwater. Granular activated carbon has long been used to remove taste and odor causing organic chemicals from drinking water supplies and an extensive range of organic compounds from industrial wastewaters. This ability to remove specific organic compounds has made GAC a logical choice to treat groundwater contaminated with identifiable organic compoounds. Since the early 1970's, Calgon Carbon Corporation has had direct involvement in over 50 successful applications of adsorption in the treatment of contaminated groundwater.

As with air stripping, specific organic compounds have characteristics which affect their adsorbability on activated carbon. Adsorbability is enhanced by increasing molecular weights, decreasing solubility in water, and the presence of functional groups such as chlorine substitutions or aromatic structures.

The following list shows the influence of these factors, with adsorbability identified as the capacity of activated carbon for the contaminant at a constant concentration of 500 ppb.

Compound	Molecular Weight	Solubility (mg/l)	Adsorbability (mg/g Carbon)
Tetrachloroethylene	166.0	150.	110.0
Trichloroethylene	131.5	1,000.	42.0
1,1,1-Trichloroethane	133.5	4,400.	17.0
1,1-Dichloroethane	99.0	5,100.	5.0

As adsorption is an equilibrium process, the concentration of the compound will affect the capacity of the activated carbon for the contaminant.

The ability of activated carbon to remove specific organic compounds makes it an effective technology to use alone, or as a complementary technology with air stripping.

Granular activated carbon can also remove organic compounds from gases, and has historically found application in solvent recovery operations, control of industrial air emissions and elimination of odors from gas discharges from waste water treatment plants. As vapor phase control with GAC has long been an accepted treatment technology, it has

found acceptance as a means to remove organic compounds from air stripper off-gas to insure that they are not returned to the environment.

OFF-GAS TREATMENT WITH GRANULAR ACTIVATED CARBON

The capacity of granular activated carbon to adsorb VOC's from air stripper off-gas is dependent on physical and chemical characteristics of the organic compounds, their concentration in the gas stream, and the temperature, pressure and humidity of the gas. The characteristics of compounds which influence their adsorbability on carbon from a gas stream are similar to those which influence adsorption from water, namely their molecular weight, functional groups or structures, and their vapor pressure, which can be viewed as "solubility" in the gas. Any organic compound that exerts a vapor pressure and exhibits other adsorptive characteristics is a viable candidate for vapor phase adsorption on activated carbon.

Figure 1 contains single component vapor phase isotherms for some typical VOC's at ambient temperature and pressure. If the partial pressure is divided by 14.7 psia, then the adsorptive capacity can be seen to increase with increasing concentration. These general curves are fairly accurate for partial pressures greater than 0.001 psia or concentration greater than 50 ppm and a relative humidity less than 50%.

As can be seen from the isotherms, compounds with higher molecular weights and higher boiling points generally have a greater adsorptive capacity. The higher the temperature, however, the lower the capacity, as the compound will exhibit a greater volatility and attraction to the gas stream.

The vapor discharge from an air stripper typically has a relative humidity close to 100%. This condition may decrease the adsorptive capacity in the range of 15 to 50% due to the presence of water in the gas stream, therefore, either heating of the air to reduce the relative humidity or increasing the carbon bed depth may be necessary.

The design of a granular activated carbon system is based on the air volume rate, the concentration and types of VOC's, pressure drop through the system and the linear velocity through the carbon bed. Normal vapor phase system designs utilize a linear velocity between 20 and 100 feet per minute with pressure drops of 0.6 to 5.5 inches W.C. per foot of bed with 2 to 3 feet of activated carbon bed depth to contain the mass transfer zone. A principal objective in the design of a vapor phase system is to minimize the pressure drop so as to lower fixed energy costs for the motive air system. It is also desired to optimize the system design for maximum carbon utilization so as to minimize the operating cost for carbon replacement or regeneration. One method to obtain this optimization in an air stripper off-gas treatment system is to minimize the air-to-water ratio of the air stripper to minimize the air volume

rate and maximize the organic concentration for a higher adsorptive capacity.

The lower air flow rate will allow the use of smaller vapor phase adsorbers which minimizes the capital costs for the system. If the VOC removal rate is maintained, the lower air rate will also increase the concentration of VOC's in the off-gas. As adsorption is an equilibrium process, this increased concentration will increase the capacity of activated carbon for the contaminants and lower the carbon usage rates.

Changes can often be made in air stripper designs to compensate for the lower air-to-water ratios and still obtain the desired VOC removal. If the air stripper can be increased in height, additional packing bed depth will provide for additional transfer units at the lower air rate. If additional packing depth is not feasible, smaller packing can be used to lower the height of a transfer unit and obtain more transfer units at the same bed depth. Another design alternative with lower air rates is to heat the influent water to increase the relative volatility of the VOC.

<u>Non-regenerable Vapor Phase Adsorption Systems</u>

Our experience indicates that a non-regenerable system may be the more economical choice when the carbon bed life is expected to be greater than three months. In a non-regenerable system, the VOC contaminated air is passed upflow through a bed of GAC and discharged. After a period of time, the mass transfer zone will reach the top of the bed and VOC's will be present in the exhaust. The GAC system will be taken off-stream, the spent carbon removed, and a new bed of carbon installed to resume treatment.

An example of a non-regenerable GAC adsorption system to remove VOC's from air stripper exhaust is shown in Figure 2. The vapor phase system was designed for an air volume of 5,350 cfm, 50% RH and a 90% removal of 15 pounds per day of VOC's.

The humidity was reduced by raising the air temperature 30^{O}F with a 250 MBTU per hour natural gas fired heater. The goal of humidity reduction was to increase the capacity of carbon for the VOC's and extend the bed life. The VOC concentration in the off-gas was maximized by using a low air-to-water ratio of 20 to 1, and compensating in the tower design by providing 40 ft. of packing depth. The exhaust gas from the air stripper was split between two 10-foot diameter carbon adsorbers each containing 314 ft.^{3} of BPL 4x6 GAC (a product of Calgon Carbon Corporation, Pittsburgh, PA) in 4 ft. deep beds and operated at 70 fpm linear velocity. The carbon was expected to be changed out three times per year, based on design conditions.[6]

The installed capital cost for non-regenerable off-gas treatment systems will generally be in the range of $30 to $50 per cfm of gas to be treated. This system would include ductwork from the air stripper, FRP

adsorber vessel(s) with exhaust stack(s) and the initial fill of granular activated carbon. The operating expense of a non-regenerable system includes the electrical costs for increased blower pressure, replacement costs for fresh GAC and costs for disposal of the spent GAC.

Regenerable Vapor Phase Adsorption Systems

In regenerable systems, the GAC is regenerated in place with steam, inert gas or incinerator combustion gas. This process is employed when the VOC level is high, VOC's are to be recovered, or the GAC exhaustion rate is high.

Regenerable systems normally operate with two or more adsorbers in parallel. One or more vessels are in service to adsorb VOC's while a single vessel is being regenerated or waiting to replace a spent bed. For regeneration of GAC containing VOC's, a temperature of 220°F or greater is required to drive the VOC's from the carbon surface so the adsorptive capacity is recovered. In the case of steam regeneration systems, treatment of the carbon bed with 1.0 to 1.5 pounds of steam per pound of GAC over a one hour period will usually effect the regeneration. The organic compounds and steam are cooled in a condensor and collected for disposal or reuse. Present disposal costs are approximately $1.40 per gallon for off-site destruction. After regeneration, the carbon is cooled before being returned to the adsorption cycle. Depending upon the nature of regeneration and cycle scheduling, there may be a 10% continual VOC discharge to the atmosphere with this type of system.

The capital cost for an installed regenerable system can be in the range of $70 to $100 per cfm of gas to be treated. A regenerable system will include ductwork from the air stripper, coated steel or alloy adsorber vessels, condensor, condensate collection tank and automated valves and controls to operate the regeneration cycle. The design may also need to incorporate special metals or coatings to prevent corrosion by the chlorinated organic compounds. The operating expense of a steam regenerable system includes electrical costs, steam supply costs, cooling water costs and condensate disposal cost. There will also be a cost of periodic carbon replacement when the regeneration process ceases to effectively return adsorptive capacity to the granular activated carbon.

Hot inert gas regeneration provides for a higher purity solvent for recovery or for direct incineration. The operating cost will probably be higher due to the cost of the inert gas supply, if it is not part of the process. At these elevated temperatures, gas with a low oxygen content is necessary, to prevent combustion of the carbon media or adsorbates.

A regenerable system using an incinerator can be a viable technology. Inert gas is provided by an incinerator in the form of combustion gas to regenerate the carbon, with heat recovery of the unused portion. The inert gas with VOC's exiting the carbon bed is then recycled to augment the fuel to the incinerator, which provides for complete destruction of the organic contaminants. The incinerator

exhaust gas provides a higher temperature regenerant medium, providing for a faster and more complete regeneration of the granular carbon. The incinerator also eliminates the need for off-site services for contaminant disposition.

LIQUID PHASE TREATMENT WITH GRANULAR ACTIVATED CARBON

As mentioned previously, adsorption utilizing granular activated carbon is an effective means to remove specific organic compounds from water. The basic evaluation technique to determine the applicability of adsorption is the single component adsorption isotherm test. The adsorption isotherm is a batch test designed to determine the relationship between the concentration of the contaminant and the capacity of the carbon to adsorb it. Isotherms are useful in determining preliminary carbon usage rates and in comparing the adsorption characteristics of different species at different levels of concentration or a different pH value, for example. Single component liquid phase isotherms for typical VOC's are shown in Figure 3.[7]

More testing is usually required, if the process must remove a mixture of contaminants or if a more accurate prediction of carbon usage rates is required. A scaled column test to evaluate contact time and contaminant breakthrough behavior is usually the best method to define system design and operating parameters. With groundwater, however, the scaled column test may take considerable time and expense (analytical) to complete the study. In response to this need, Calgon Carbon Corporation developed mathematical models of adsorption kinetics to allow use of extremely small columns (2mm I.D.) and rapid testing so that a scaled column test requiring months can be compressed into a matter of days. This Accelerated Column Test (ACT) has been used on groundwater systems, with data published for removal of chloroform[8], 1,1,1-trichloroethane and 1,1-dichloroethane.[7]

Treatment Of Air Stripper Effluent

Although air stripping technology can obtain 99% removal of many of the VOC's, the residual contaminant level may still be unacceptable for potable water use. In other cases, non-volatile contaminants such as phenols or pesticides may be present in air stripper effluents. In these instances, treatment of the air stripper effluent with granular activated carbon is both effective and economical.

The use of air stripping as pretreatment to a carbon adsorption system has several advantages. The carbon adsorption system will be able to maintain the desired effluent quality in spite of flow and contaminant concentration variations that would affect air stripping performance. Air stripping will also reduce the level of organic contaminants for which activated carbon has a lower capacity, thereby significantly lowering the usage rate of GAC. The reduction of VOC's into the low ppb range will also allow the use of lower cost single stage adsorption equipment to further optimize treatment costs. In some instances, the

effect of the lower carbon usage rate and less elaborate air stripping system may make the combined system more cost effective than the use of individual processes.

In one typical application, a contaminated groundwater was being treated with a simple air stripper followed by carbon adsorption. The following table summarizes the performance of this system:

Combined System Performance

Contaminant	TCE	PERC	II DCE	II DCA	III TCA
Influent, ppb (avg.)	42	80	92	256	544
Air Stripper Effluent; (ppb (avg.)	4	8	7	116	73
% Removal; Air Stripping	90.5	90	92	55	87
Carbon Effluent; ppb (at 80 days)	—	—	—	23	10
% Removal; Carbon	100	100	100	58	88.5
% Removal; Overall	100	100	100	91	98

Based upon 80 days operation, the carbon usage rate was 1.13 pounds per 1,000 gallons. If the air stripper performance could be improved, further reduction of the dichloroethane and trichloroethane would result in extended carbon usage. Even with a more efficient air stripper, the carbon adsorption system would provide valuable insurance against contaminant concentrations excursions with an effluent of desired quality.

Treatment of Air Stripper Influent

If the limitation on air stripper use is the emission of only a small amount of organic compounds over a given time period, then a concept which can be considered is pretreating the air stripper feed water with granular activated carbon.

In this design, the air stripper essentially acts as a "second stage" to the adsorption units, allowing more complete utilization of carbon adsorptive capacity. As the more poorly adsorbed VOC's exit the carbon adsorber, the air stripper will remove them from the water stream. When the VOC level exiting the adsorption system approaches the air discharge limitation, the granular activated carbon is replaced.

The advantage of this approach is that groundwater contaminantion may include small amounts of VOC's such as vinyl chloride or methylene chloride that may be degradation components of the prime contaminants. The levels of such contaminants may exceed the desired level for water quality, but on a total weight basis would be allowable as air emissions. The carbon adsorption system can be allowed to effectively remove the higher molecular weight contaminants, while the air stripper removes the lower molecular weight contaminants without requiring off-gas treatment

systems. The final advantage is that the liquid phase carbon can be thermally regenerated, allowing for complete destruction of the contaminants.

This approach may be particularly useful when confronted with a mixture of organic contaminants, and when operation of a regenerable gas phase system may be unfeasible. A typical application might include the following:

Typical Combined System Performance

Contaminant	PERC	TCE	IIDCE	Vinyl Chloride
Influent; ppb	400	300	80	40
Carbon Effluent; ppb	—	—	80	40
Air Stripper Effluent, ppb	—	—	<1	<1

Air Emission Rate (500 gpm) = 0.03 lbs./hour
Carbon Usage Rate (500 gpm) = 0.24 lbs./1,000 gallons

Use of Activated Carbon Adsorption Alone

The use of granular activated carbon for VOC removal from groundwater still remains a viable treatment technology regardless of air stripping capabilities. The capability of GAC to maintain effluent quality in spite of flow variation, changes in contaminant mix or levels, and it's ability to be thermally regenerated insuring destruction of contaminants are advantages that air stripping systems do not have.

In previous surveys on the use of GAC in groundwater treatment, we reported that carbon usage rates of less than 0.5 lbs. of GAC per 1,000 gallons treated were observed in 9 of 12 applications where VOC's were present at ppb levels. Most of these applications utilized single- stage systems to minimize capital expense. For these applications, treatment costs, including equipment and carbon expense, was estimated to be in the range of 22-55 cents per 1,000 gallons.[9]

In situations where contamination was present in the ppm range, two-stage systems were frequently utilized to optimize carbon usage. In 10 of 19 applications, the survey reported carbon usage rates of 1.54 lb. GAC per 1,000 gallons or less. For all 19 applications resultant treatment costs ranged from 48 cents to $2.52 per 1,000 gallons.[9]

Although not an economical choice for all groundwater contamination treatment situations, when GAC is properly evaluated and applied, it can not only be highly effective, but economically attractive.

CONCLUSION

With proper design and application, the use of carbon adsorption in groundwater treatment can be an effective and economical technology.

When combined with air strippers for water treatment, carbon adsorption can provide for improved overall system performance at optimum carbon usage rates and treatment costs. The use of carbon adsorption to remove contaminants from air stripper off-gas is also a proven technology, and depending on usage rates, on-site regeneration techniques may improve the cost effectiveness.

In order to make a proper evaluation of these systems, however, the specific problem and long-term solution must be well defined. The amount and nature of contaminants, the end use of the water, air pollution concerns, operational considerations and economics associated with the capital and continuing operation are important factors in selecting the best treatment system to address groundwater contamination.

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FIGURE 1

VAPOR PHASE ISOTHERMS
ADSORPTION ON BPL CARBON
AT 77^{0}F, RELATIVE
HUMIDITY <40%

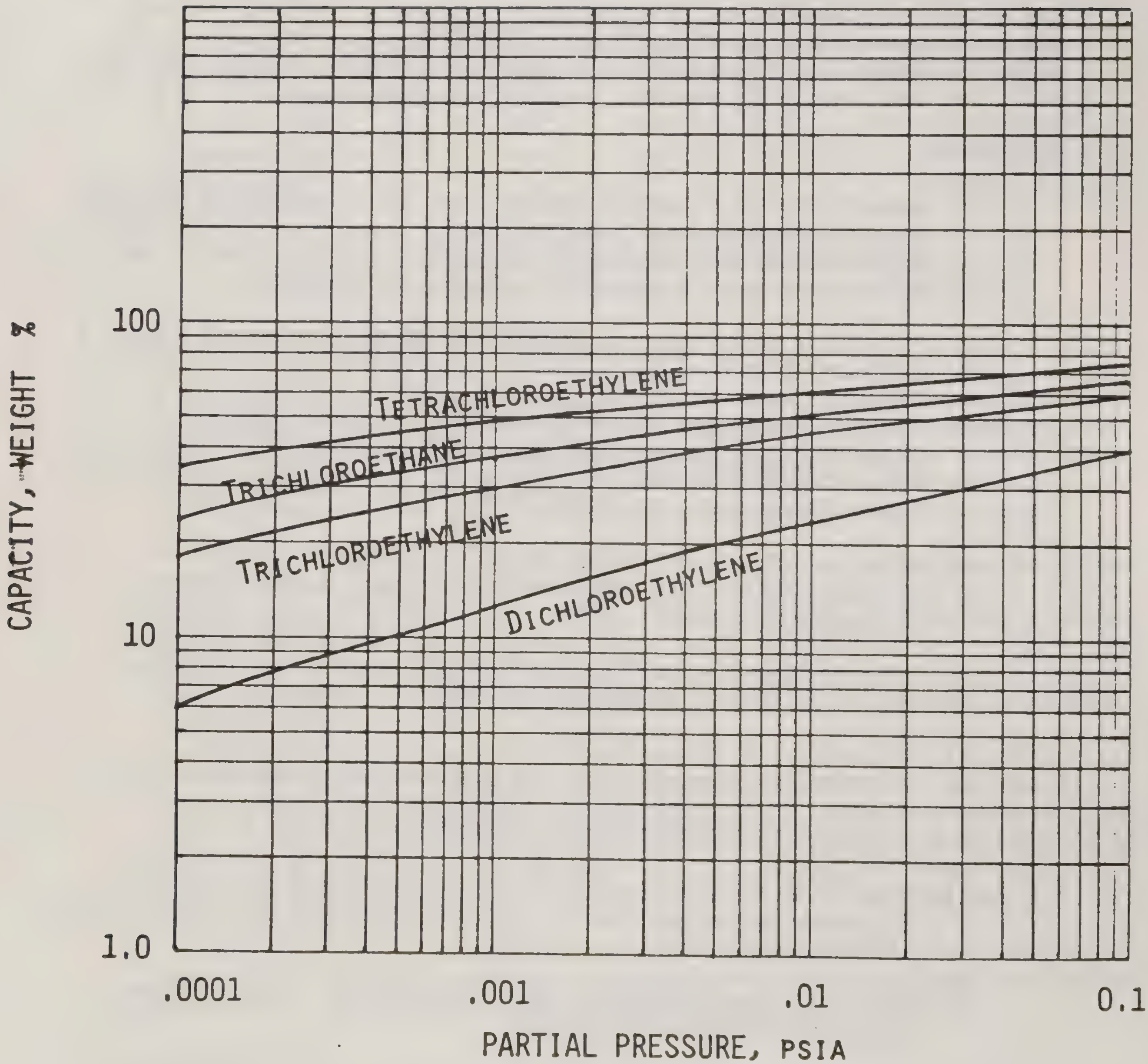


FIGURE 2

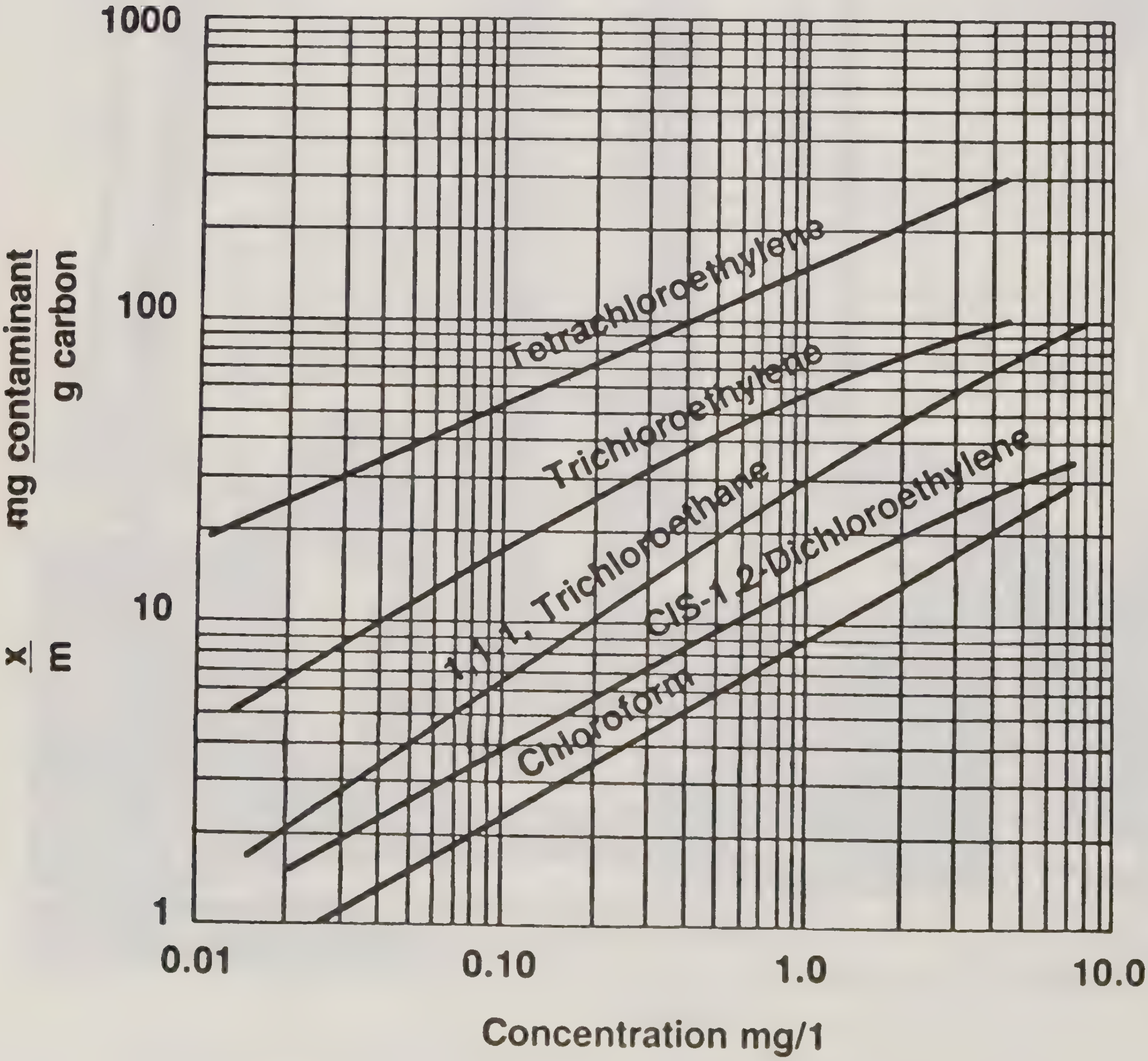
This air stripping system treats groundwater from blocking wells, removing contamination from the aquifer to protect potable water wells. The packed tower air stripper is 10 feet in diameter and contain 40 feet of packing to treat 1,100 gpm. The vapor phase carbon adsorbers (foreground) each contain 314 cubic feet of carbon to treat 5,350 cfm off-gas from the air stripper.

FIGURE 3

CARBON ADSORPTION ISOTHERMS

Basis

Sample volume — 137 mls
Temperature — Ambient
Agitation Time — 20 hours
Carbon — Filtrasorb 300



PCB-Contaminated Soil Treatment in a Transportable Circulating Bed Combustor

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ABSTRACT

A trial burn of PCB-contaminated soils was completed in GA Technologies' transportable Circulating Bed Combustor (CBC). Over 4000 pounds of soil containing 1% PCB were treated in three identical 4-hr runs at 1800°F. The results showed excellent compliance with U.S. Environmental Protection Agency (EPA) Toxic Substances Control Act (TSCA) requirements. Destruction and removal efficiencies (DREs) were greater than 99.9999% and PCB in combustor ash was less than 200 ppb. No chlorinated dioxins or furans were detected in the stack gas, bed ash or fly ash. In addition, no significant concentrations of other Products of Incomplete Combustion (PICs) were detected. Combustion efficiencies were greater than 99.9%, with CO concentrations less than 50 ppm and NO_x concentrations less than 75 ppm. Particulate emissions were generally below 0.08 grain/dscf and HCl emissions were maintained below 4.0 lb/hr by introducing limestone directly into the combustor. These results led to the first TSCA permit for a transportable incinerator which can be used in all ten EPA regions. This demonstrates that the CBC is an environmentally acceptable means of treating contaminated soil containing PCB and other organic wastes. In addition, the high thermal efficiency, the absence of afterburners or scrubbers, and the use of simple feed systems make CBC treatment competitive with soil removal and transport to landfills and other potential treatment/disposal options.

INTRODUCTION

Polychlorinated biphenyls, or PCBs, have perhaps received more scrutiny than any other hazardous chemicals found in waste sites around the country. This group of 209 synthetic chlorinated organic compounds found wide use as a dielectric fluid in utility transformers and capacitors, and as a high-temperature heat transfer medium [1]. However, because of their exceptional resistance to degradation in the

biosphere and apparent toxicity, the manufacture and sale of PCBs were banned in 1976 for virtually all purposes. The control, treatment and disposal of PCBs was mandated by TSCA and is currently handled through EPA's Office of Toxic Substances.

Until recently, it has been common practice to remove contaminated soils for burial in a secured landfill. However, this option is becoming less desirable as landfill costs escalate, the number of available landfill sites drop, and generators or potential responsible parties (PRPs) become increasingly aware of retained liability associated with the contaminated soils, even in a secured landfill. Treatment of PCB-contaminated soil by incineration in the CBC can eliminate or significantly reduce the potential liability of generators or PRPs at a cost competitive with landfill prices.

The use of CBC technology for hazardous waste treatment builds on over 15 years experience at GA in the design, development and operation of fluidized bed combustors. In 1980 GA and Ahlstrom of Finland formed Pyropower Corporation to supply CBCs for the U.S. boiler market. These units are designed to burn a wide variety of fuels such as coal, peat, wood, municipal wastes and oil. Over 25 units are operating or under construction worldwide. Three units are currently in operation in the U.S. In 1983, GA began concentrating its efforts on the application of CBC technology to incineration of hazardous wastes. Table 1 presents examples of wastes that have been burned in the CBC during this time. Successful treatment of this diversity of wastes provided assurance that PCBs could be destroyed in a CBC at a lower temperature than used in conventional incinerators.

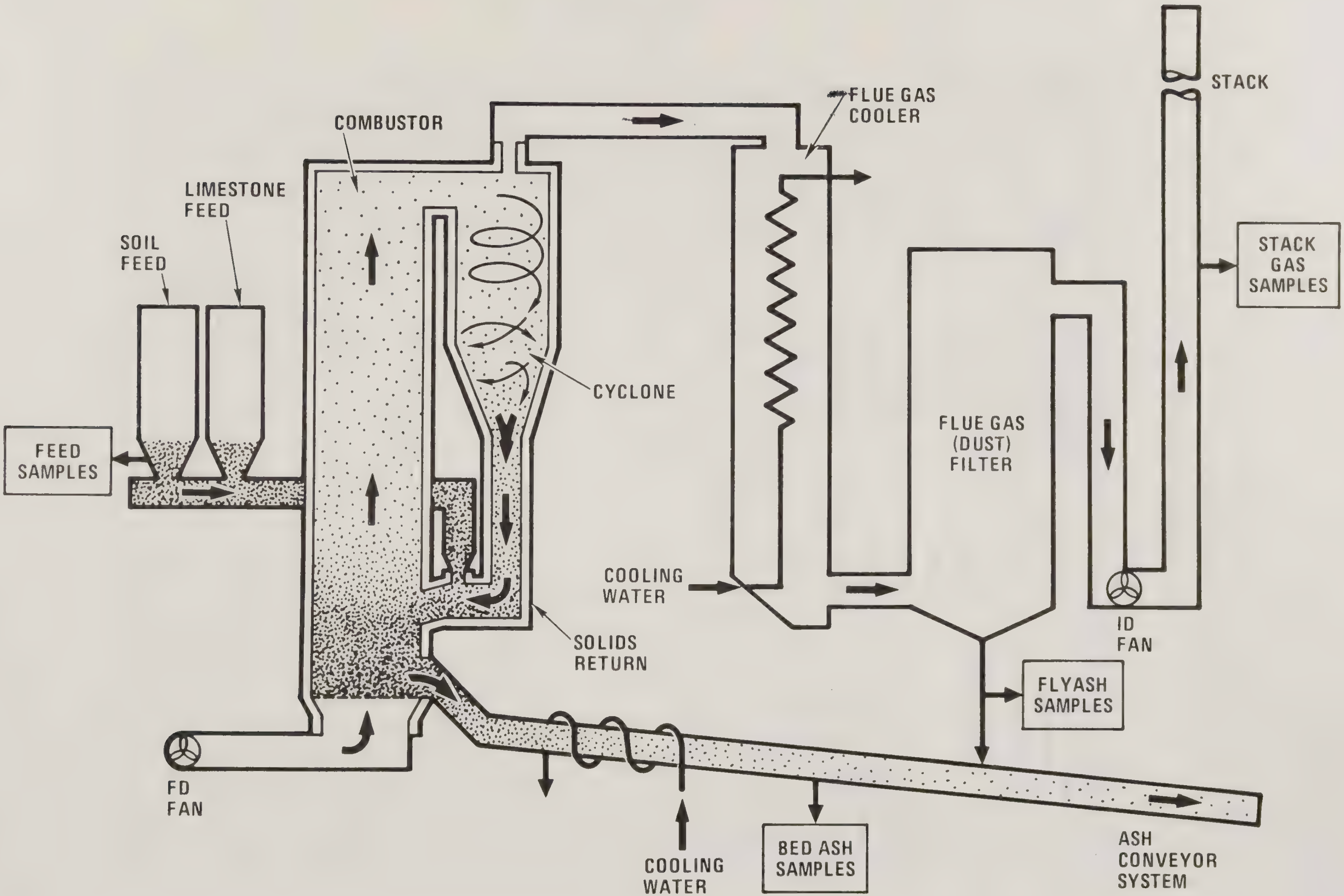
CBC DESCRIPTION

The CBC is a new generation of incinerator that uses high velocity air to entrain circulating solids in a highly turbulent combustion loop. This design allows combustion along the entire length of the reaction zone. Because of its high thermal efficiency, the CBC is ideally suited to treat feed with low heat content, including contaminated soil. Figure 1 shows the major components of a CBC for soil treatment. Soil is introduced into the combustor loop at the loop seal where it immediately contacts hot recirculating soil from the hot cyclone. Hazardous materials adhering to soil are rapidly heated when introduced into the loop and continue to be exposed to high temperatures throughout their residence time in the CBC. Upon entering the combustor, high velocity air (14 to 20 ft/s) entrains the circulating soil which travels upward through the combustor into the hot cyclone. Retention times in the combustor range from 2 seconds for gases to ~30 minutes for larger feed materials (<1.0 in.). The cyclone separates the combustion gases from the hot solids, which are returned to the combustion chamber via a proprietary non-mechanical seal. Hot flue gases and fly ash pass through a convective gas cooler and on to a baghouse filter where fly ash is removed. Filtered flue gas then exhausts to the atmosphere. Heavier particles of purified soil remaining in the combustor lower bed

Table 1

Circulating Bed Test Results

Waste	Form	Destruction Efficiency, %	HCl Capture, %	Ca/Cl_2 Ratio
Carbon Tetrachloride	Liquid	99.9992	99.3	2.2
Freon	Liquid	99.9995	99.7	2.4
Malathion	Liquid	>99.9999	-	-
Dichlorobenzene	Sludge	99.999	99	1.7
Aromatic Nitrile	Tacky solid	>99.9999	-	-
Trichloroethane	Liquid	99.9999	99	1.7


COMBUSTOR
LIMESTONE FEED
SOIL FEED
FEED SAMPLES
CYCLONE
SOLIDS RETURN
FD FAN
COOLING WATER
BED ASH SAMPLES
FLUE GAS COOLER
COOLING WATER
FLUE GAS (DUST) FILTER
FLYASH SAMPLES
STACK
STACK GAS SAMPLES
ID FAN
ASH CONVEYOR SYSTEM

are slowly removed by a water cooled ash conveyor system. As a consequence of the highly turbulent combustion zone, temperatures around the entire loop (combustion chamber, hot cyclone, return leg) are uniform to within /50°F. The uniform low temperature and high solids turbulence also help avoid ash slagging encountered in other types of incinerators.

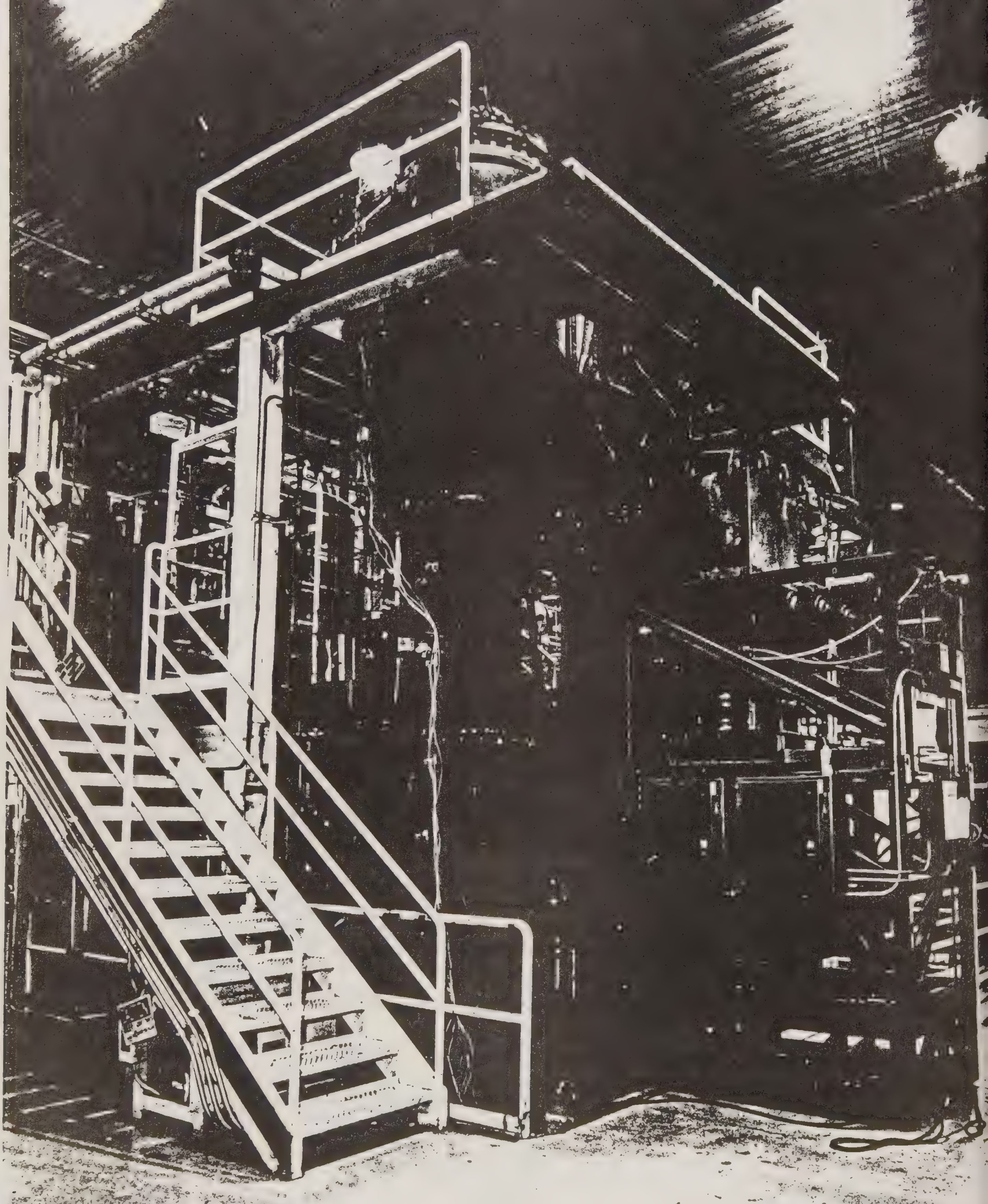
Acid gases formed during destruction reactions are rapidly captured in situ by limestone added directly into the combustor. The reaction of HCl, released during PCB incineration, and limestone forms dry calcium chloride, a benign salt. The rapid combustion and quick neutralization of the acid gases within the combustion chamber eliminates the need for afterburners and add-on scrubbers to complete destruction and acid gas capture, respectively. Emissions of CO and NO_x are controlled to low levels by excellent mixing, relatively low temperatures (1450 to 1800°F), and staged combustion, achieved by injecting secondary air at higher locations in the combustor. Because of its efficient combustion and highly turbulent mixing, the CBC is capable of attaining required DREs for both hazardous wastes (99.99%) and toxic wastes (99.9999%) at temperatures below those used in conventional incinerators (typically >2000°F).

TEST DESCRIPTION

A variety of requirements are imposed prior to and during a PCB trial burn [2]. The key target of a trial burn is to ensure that PCB DREs are >99.9999% at the operating conditions chosen for the incinerator. In addition, the concentration of PCB in ash from the unit must not exceed 2 ppm. The potential formation of PICs is also carefully evaluated, with particular attention given to polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (PCDFs). The combustion efficiency of the unit must be >99.9% and particulate emission must not exceed 0.08 grain/dscf.

The CBC trial burn was carried out in GA's transportable unit, shown in Figure 2. Soil treated in the test was obtained from a former chemical processing site known to contain pockets of PCB up to 6000 ppm, as well as other organic and inorganic wastes. In order to ensure that the CBC would be permitted to treat all likely site concentrations of PCB, uncontaminated soil from the site was "spiked" with liquid PCB to 10,000 ppm. Spiking was carried out by blending a 50:50 commercial mixture of PCB "1248" and trichlorobenzene with a ribbon blender in 1000 lb lots. Approximately 4000 lb of soil was spiked for the three burns required by the TSCA trial burn permit.

While the CBC was maintained at 1800°F using natural gas as the auxiliary fuel, several barrels of clean site soil were introduced into the CBC prior to the addition of spiked soil. During this time all



operating parameters and system components were confirmed to be in the required operating ranges. Process parameters monitored included:

- Temperature around the loop
- Pressure drop across the loop
- Soil feed rate
- Primary air flow
- Secondary air flow
- Loop seal air flow
- Total air flow
- Methane flow
- CO concentration
- CO_2 concentration
- Excess oxygen level
- NO_x concentration

Spiked soil was pneumatically transported to a bunker and screw feeder. Soil feeding, limestone addition and stack gas monitoring were started simultaneously. An EPA Modified Method 5 sample train [3] was used to sample stack gas emissions. In addition, a separate Volatile Organic Sampling Train (VOST) [4] was used to sample for volatile organic PICs. Feed, bed ash and fly ash samples were also gathered throughout the test (see Figure 1 for sample port locations). Three identical tests of spiked soil (4 hours each) were carried out over two days in late May 1985. Each test was observed and/or audited by EPA personnel or representatives. All feed, ash and stack gas samples were subsequently analyzed for PCBs, PCDDs and PCDFs. Fly ash, bed ash and stack gas samples were also analyzed for other PICs (both volatile and semivolatile). Stack gases were analyzed for fly ash and chloride release as well.

RESULTS

Table 2 presents a summary of the trial burn operational data and test results gathered during the tests. Near-identical conditions were maintained for each of the tests. In each case PCB DREs were well in excess of the EPA-required 99.9999%. PCB concentration in the bed ash and the fly ash did not exceed 200 ppb. No PCDDs or PCDFs were detected in the stack gas, bed ash, or fly ash. Combustion efficiencies were greater than 99.9% and acid gas release was well below the required 4 lb/hr. Particulate emissions were generally less than the required 0.08 grain/dscf. Only the grain loading from the first test, obtained from a 2-hr makeup test after the completion of Tests 1 through 3, showed a value slightly higher than the limit. This is attributed to

TABLE 2

PCB Trial Burn Operational Data and Test Results

Parameter	TSCA Requirement	Test Number 1	2	3
Test Duration, hr	~4	4	4	4
Operating Temperature, °F	-	1800	1800	1800
Soil Feed Rate, lb/hr	-	328	412	324
Total Soil Feed, lb	-	1592	1321	1711
PCB Concentration in Feed, ppm		11,000	12,000	9,800
DRE, %	>99.9999	99.999995	99.999981	99.999977
PCB Concentration				
- Bed Ash, ppm	<2	0.0035	0.033	0.186
- Fly Ash, ppm	<2	0.066	0.0099	0.0032
Dioxin/Furan Concentration				
- Stack Gas, pp		ND[(a)]	ND	ND
- Bed Ash, ppm	-	ND	ND	ND
- Fly Ash, ppm	-	ND	ND	ND
Combustion Efficiency, %	>99.9	99.94	99.95	99.97
Acid Gas Release, lb/hr	<4.0	0.16	0.58	0.70
Particulate Emissions, grain/scf (dry)	<0.08	0.095[(b)]	0.043	0.0024
Excess Oxygen, %	>3.0	7.9	6.8	6.8
CO, ppm	-	35	28	22
CO_2, %	-	6.2	6.0	7.5
NO_x, ppm	-	26	25	76

[(a)] ND = Not detected.

[(b)] Derived from 2-hr makeup test.

off-normal process conditions for the baghouse, i.e., excessive blowback air pressure along with a higher-than-normal number of blowback cycles. Nitrogen oxides and CO levels remained low as a result of the staged combustion utilized in the CBC and the relatively low combustion temperature (1800°F). These results demonstrate that the CBC is an effective means to destroy PCBs contained in a soil matrix, without the need for high temperatures, afterburners or wet scrubbers. In particular, the absence of undesirable combustion byproducts help ensure that effective treatment of soil can be obtained in an environmentally acceptable manner.

These results confirm the design of GA's transportable CBC shown in Figure 3. The combustor and all other plant components are designed as modular units which can be transported by truck or rail. These units are assembled at the site into an operating unit in four to six weeks. The major components of this CBC plant include the combustor loop, feed system, and pollution control and air induction equipment. GA's 36-inch transportable CBC is capable of processing up to 4 t/hr of dry soil on a 24-hour basis, requiring an operating crew of only two persons per shift. Soil treatment costs may be as low as ~$100/ton for a large site. For smaller sites or sites having unique treatment requirements, costs may approach ~$400/ton.

CONCLUSION

The results of the PCB soil trial burn in GA's CBC demonstrate compliance with EPA TSCA requirements. The CBC is now one of only seven incinerators nationwide permitted to burn PCB, and one of only two permitted transportable incinerators, the other being the EPA rotary kiln. It is the first transportable incinerator to be permitted in all ten EPA regions. Stack emissions from the CBC are well within regulatory requirements and bed ash and fly ash contain PCBs well below the regulatory requirements. The superior thermal efficiency, high throughput and small staffing requirements of the CBC provide a soil treatment option that is cost competitive with landfill dispoal while at the same time reducing overall liability of the generator or PRP.

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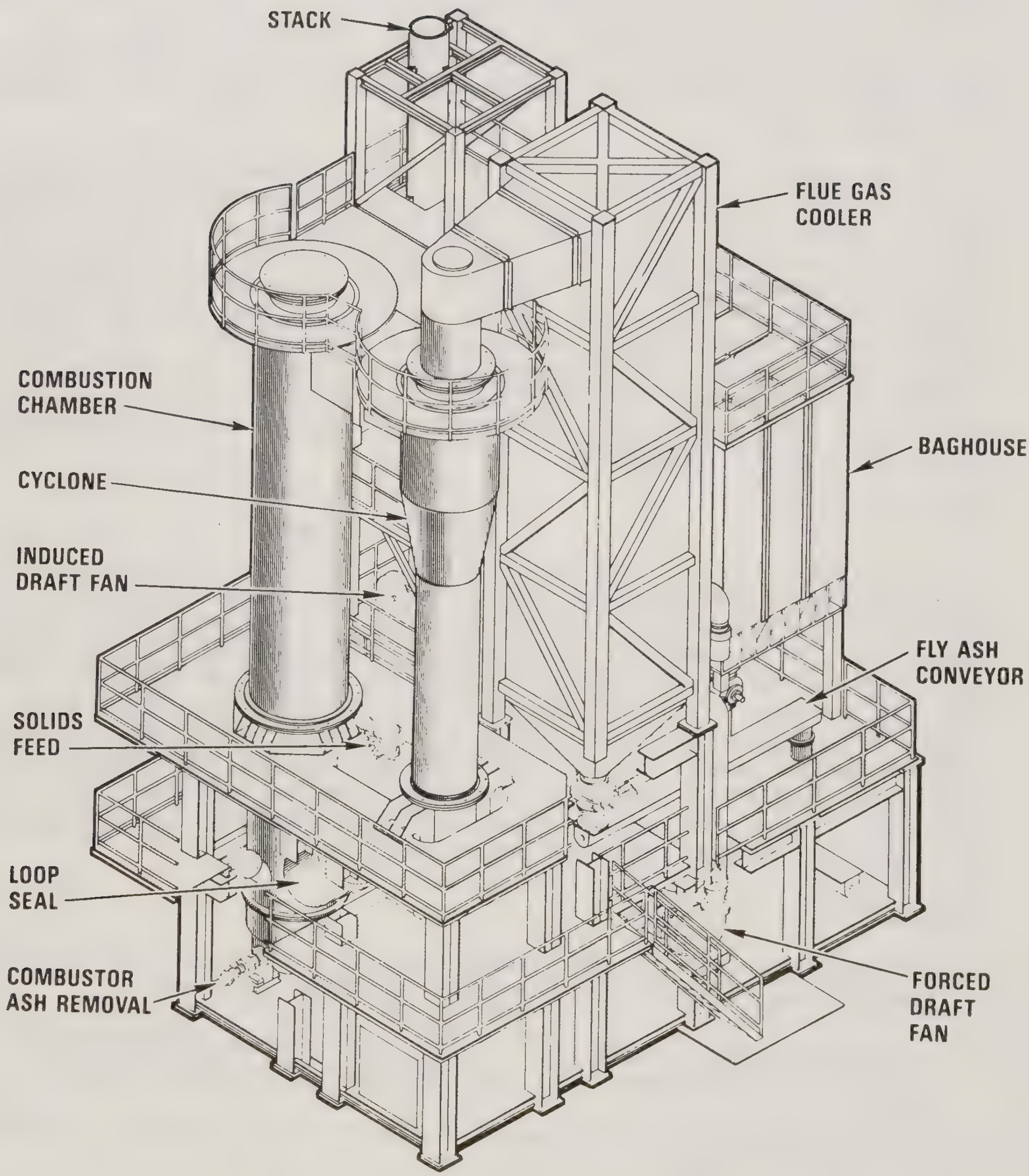
STACK
FLUE GAS COOLER
COMBUSTION CHAMBER
BAGHOUSE
CYCLONE
INDUCED DRAFT FAN
FLY ASH CONVEYOR
SOLIDS FEED
LOOP SEAL
COMBUSTOR ASH REMOVAL
FORCED DRAFT FAN

OPERATION OF CONTROLLED AIR INCINERATORS AND DESIGN CONSIDERATIONS FOR CONTROLLED AIR INCINERATORS TREATING HAZARDOUS AND RADIOACTIVE WASTES

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ABSTRACT

The intent of this paper is to review the basic theory and design philosophies of the so-called Controlled-Air Incinerator and to examine the features of this equipment which make it ideally suited to the application of low-level radioactive waste disposal. We will also present special equipment design considerations for controlled air incinerators treating hazardous and radioactive wastes.

HISTORICAL COMMENTS

Over the years, two distinctive types of incineration equipment have evolved. One type which we will refer to as "excess air" units and typified by the large municipal facilities have been around for decades..the These units often operate at relatively high air flow conditions beneath fire bed, the excess air being utilized to cool one or more types of hearth grate systems. As a result of this hearth turbulence most of these units require auxiliary cleanup equipment for particulate emission control. These units also consist essentially of one large furnace although different combustion zones and air distribution areas occur within this furnace.

In the 1960s a number of manufacturers introduced the so-called "controlled-air" incinerator. Other synonyms for this equipment have included "starved-air," "pyrolytic" and "stuff-and-burn" incinerators. These units are presently manufactured in a capacity range of approximately fifty (50) to five-thousand (5000) pounds per hour. Controlled-air incinerators consist of two distinctive chambers, an ignition or primary chamber and an upper secondary or combustion chamber. These chambers may be of a circular or rectangular cross section depending upon the manufacturer. The general theory of operation of these units is to maintain the lower chamber at less-than-stoichiometric air conditions to minimize particulate entrainment and for temperature control. The lower chamber serves primarily as a volatilization chamber. Volatiles generated in the lower chamber are then drawn into the secondary chamber where excess combustion air is injected under turbulent conditions to achieve final combustion. The upper combustion chambers are generally sized volumetrically for gas retention times of 0.25 to 2.0 seconds depending upon the waste chemistry, manufacturer and specification requirements. The great advantage of controlled-air incinerators has been that a wide variety of organic wastes may be destroyed via combustion with extremely low particulate emissions. This capability makes the controlled-air unit

ideally suited for low-level radwaste destruction where maximum limits on radiological releases to the atmosphere are of priority importance. This obviously is also of great advantage even in those systems requiring off-gas treatment in that the useful lives of primary filter elements are extended.

It is to this latter type of incinerator, the controlled-air unit, that this paper is addressed.

CHEMISTRY OF COMBUSTION

So as to fully understand the principle of controlled air incineration, it is important that we become familiar with some basic chemistry of waste materials. All commonly encountered organic waste may be characterized as consisting primarily of carbon (C), hydrogen (H) and oxygen (O). Other elements found in lesser degree are sulfur (S), nitrogen (N) and chlorine (Cl). For our discussion here, we will make certain simplifications and concern ourselves with the three most abundant constituents, namely, carbon, hydrogen and oxygen.

In incineration, combustion occurs according to the following chemical equations:

$$\underset{(12\text{ lbs.})}{C} + \underset{(32\text{ lbs.})}{O_2} = \underset{(44\text{ lbs.})}{CO_2} \qquad (1)$$

$$\underset{(2\text{ lbs.})}{H_2} + \underset{(16\text{ lbs.})}{1/2\ O_2} = \underset{(18\text{ lbs.})}{H_2O} \qquad (2)$$

Carbon and hydrogen combine with oxygen of the combustion air to form carbon dioxide and water vapor respectfully. Any oxygen in the waste passes through the combustion process unchanged. Heat is liberated in the combustion process according to the above equations to the extent of 14,100 BTU per pound of carbon burned and 61,000 BTU per pound of hydrogen burned. The quantities of oxygen shown in equations (1) and (2) are termed "stoichiometric" or theoretical oxygen. In other words, the exact amount of oxygen required for the combustion of carbon and hydrogen is supplied. Due to inadequate mixing in commercial type equipment and temperature restrictions on the refractory, it is always customary to supply more oxygen (or combustion air) than is theoretically required so as to ensure that each carbon and hydrogen molecule is reacted to its final combustion product. The additional oxygen, or air, over and above the theoretical amount is termed "excess air."

Maximum combustion temperatures are always attained at the stoichiometric condition. As the amount of excess air is increased above the stoichiometric point, the combustion temperature is lowered. As the amount of excess air is decreased, the combustion temperature increases until it becomes maximum at the stoichiometric point.

One further fact needs to be pointed out so as to fully understand the controlled-air incinerator principle. If the amount of air is further decreased below the stoichiometric point, the temperature again decreases. A graphical representation of these combustion processes is shown in Figure 1. The simple philosophy of controlled-air incineration is to maintain primary chamber conditions to the left of the stoichiometric point while maintaining the secondary combustion conditions to the right of the stoichiometric point.

The amount of excess air provided to and its distribution within the two chambers of a controlled-air incinerator directly affects almost every operating parameter of the unit including chamber temperatures, amount of auxiliary fuel usage, ash quality, effluent compositions, refractory longevity and particulate emissions.

Of equal importance to the amount of excess air is the chemical characterization of the waste. Any waste material can be described by a "proximate analysis." A proximate analysis is simply a laboratory determination of four major components of the waste material. These components consist of the following:

Wt. % Volatile Matter
Wt. % Fixed Carbon
Wt. % Moisture
Wt. % Ash or Noncombustibles
100 %

Volatile matter is that portion of the waste which can be liberated with the application of heat only. In controlled-air incineration, the volatile matter is burned primarily in the secondary chamber upon exposure to secondary combustion air. In practice some of the volatile matter will also be burned in the primary chamber but minimization of this is desirable. Volatile matter combustion is a gas-phase reaction. Fixed carbon is the nonvolatile portion of the waste and must be burned at higher temperatures and at increased duration of exposure to so-called "underfire air," i.e., air which is introduced up through the bed of char in the primary chamber. The combustion of fixed carbon is a solid-phase reaction. Moisture is evaporated from the waste due to heat contained in the primary chamber and then passes through the secondary chamber and out of the incinerator as superheated water vapor. Ash and noncombustible remain in the primary chamber. It is primarily this component that represents the potential air pollution problem in that small micron-sized particles become entrained in the effluent combustion gases. This emission is minimized in controlled-air incinerators by maintaining nonturbulent conditions within the primary chamber from the standpoint of underfire air distribution and velocities up through the burning bed and overall gas velocities within the chamber itself.

A summary of the conditions and processes taking place within a controlled-air incinerator are shown in Figure 2.

The proximate analysis for a given waste is a useful tool for quickly estimating the conditions to be expected within a controlled-air incinerator when burning a given waste. The following general statements may be made:

1. The higher the volatile content of the waste, the greater the percent of total combustion occuring in the secondary chamber with correspondingly higher temperatures in that chamber and minimal auxiliary fuel requirements for the afterburner. This type of waste usually results in a secondary chamber temperature significantly higher than the primary chamber temperature. This waste is ideal for controlled-air incineration.

   Figure 3 is a typical representation of the temperature profile in both chambers for a highly volatile waste. Note that the temperature of the secondary chamber stays well above that in the primary chamber as long as

waste is consistently fed to the unit. When waste is no longer fed, the unit enters a so-called "burndown" condition at which time a temperature inversion normally occurs within the chambers, i.e., temperature in the primary chamber takes an upward trend during which time residual fixed carbon is burned out. Coincident with this is a decrease in the secondary chamber temperature due to the absence of volatiles. As the secondary temperature approaches the afterburner set point, the burner will fire to maintain minimum combustion tempratures until such time that the adjustable burndown cycle is complete and the unit shuts down.

It is of interest to note the periodic peaks on the temperature profiles in Figure 3. These typical peaks occur on charging and are the result of infiltration air. At these points when the charging door is open, the additional air causes a slight increase in primary chamber temperature as the result of localized burning of some volatile material in that chamber. As a result a slight temperature decrease occurs in the secondary chamber. Once the charging door closes, a reversed trend usually occurs, i.e., lower primary chamber begins to cool as a result of operation at less than stoichiometric air and the upper secondary temperature increases due to increased combustion occurring from volatile generation of the new waste charge.

2. The higher the fixed carbon content of the waste, the greater the percent of total combustion occurring in the primary chamber. Some auxiliary fuel may be required in the secondary chamber. This type of waste usually results in a secondary chamber temperature lower than the primary chamber temperature.

   Figure 4 is a typical representation of a temperature profile for high fixed carbon wastes. Note that the temperature inversion normally does not occur here in that the primary chamber is usually above the secondary temperature at all stages. Cessation of waste feeding, however, does cause the typical increase in primary chamber temperature and decrease in secondary temperature during the burndown phase.

3. The higher the moisture content of the waste, the greater the amount of heat required in the primary chamber for evaporation and heating of gases to combustion temperature. A typical example of this is Type 4, or pathological waste, which contains 85% moisture by weight. For this waste, a number of auxiliary burners are required in the lower primary chamber to provide heat for evaporation of moisture. Additional auxiliary fuel input is also required in the secondary chamber to maintain combustion temperatures at, say, 1600°F.

4. The higher the ash and noncombustible content, the greater the potential air pollution problem as concerns suspended particulate. Some auxiliary fuel input may also be required.

OPERATION

The question may well be asked, "How much excess air is required for proper incinerator operation?" The first criteria is the temperature rating of the refractory. Most controlled-air incinerators utilize a nominal 2800 to 3000°F quality refractory. Due to the presence of so-called refractory contaminants (primarily the alkaline metal oxides), it is usually not desirable to operate the secondary combustion chamber at temperatures much in excess of

2200°F on a continual basis. The enclosed Figures 5, 6, 7, 8, and 9 are theoretical plots of Combustion Temperature vs. % Excess Air and Effluent vs. % Excess Air for wastes of Types 0, 1, 2, 3, and 4 respectively. From these charts, the total excess air for a given waste to maintain a desired combustion temperature may be estimated. It is important to note that the excess air and temperature values thus obtained are "black-box" values, i.e., conditions at the point of discharge from the secondary combustion chamber.

STACK EMISSIONS

The greatest advantage of controlled-air incinerators lies in the fact that proper operation results in relatively low emission rates. Literally thousands of units have been installed by various manufacturers which operate at levels below 0.08 to 0.10 grains per standard cubic foot corrected to 12% CO_2. In the case of some wastes, corrected emissions less than 0.04 have been attained without auxiliary effluent cleanup equipment. Excessive emission rates can usually be attributed to one of the following causes:

1. High setpoint for secondary burner may not be high enough.
2. Excessive negative draft in the primary chamber.
3. Excessive infiltration air.
4. Excessive underfire air in the primary chamber.
5. Problem waste.
6. Inadequate secondary combustion air.

There are special design considerations for controlled air incinerators treating radioactive waste. A controlled air incinerator can be equipped to handle a large portion of contaminated wastes without having an offgas cleaning system.

Most wastes generated at hospitals, univerisites and research institutions are either low enough in activity level, can be decayed before incineration, or wastes can be managed and segregated to meet Nuclear Regulatory Commission and EPA effluent requirements without subsequent offgas treatment. On the other hand if nuclear power plant, DOE, DOD or TRU contaminated waste is incinerated, the radiological contaminant concentration from the discharge of the secondary chamber requires further offgas cleaning and treatment equipment. We can generally classify the first as institutional waste and the other as that from nuclear fuel production or utilization facilities and DOD facilities. In either event the controlled air incinerator should be equipped with the following recommended accessories to minimize fugitive emissions, particulate and radioisotope concentrations and maximize combustion or volatile and fixed carbon components:

1. Oversized secondary combustion chamber
2. Ash removal (internal and external)
3. Liquid injection system
4. Automatic waste feeder
5. Hearth and primary chamber steam injection
6. Modulated underfire and secondary air
7. Additional instrumentation and controls

Oversized Upper or Secondary Chamber. In order to achieve a destruction and removal efficiency of 99.99 percent, a minimum two second residence time at the maximum operation or burn rate must be maintained at all times.

Ash Removal. Remote removal of the ash after burn should be provided. Under normal operation, the ash removal should be attempted only when the incinerator has cooled down. A hydraulic ram should be provided to move the ash into the discharge opening. The ash discharge opening should be equipped with a hydraulically operated refractory lined slide gate and should have provision to discharge into a receiving receptacle.

Alternate Ash Removal (Continuous Burning). Remote removal of ash during a burn should be provided. A hydraulic ram should be provided to move the ash into the discharge opening. A high temperature screw conveyor should remove the ash from the ash discharge to a receiving receptacle.

Liquid Injection System. Liquids should be injected into the incinerator separate from the solid wastes. The system should have the capacity to transfer these fluids from a tank or drum to a nozzle mounted on the incinerator. For institutional wastes the flammable liquids will be primarily toluene and xylene of varying viscosity and heat content. The liquid injection nozzle should be capable of feeding liquids of variable viscosity and heat content at a variable rate. The injector tip should be steam cooled.

Ram Feed. The incinerator should be provided with a ram charger capable of feeding the unit during a burning cycle. It should include an air lock arrangement to minimize the introduction of air to the incinerator during charging.

Steam Injection. Steam should be injected into the primary chamber at the hearth to control temperature and to enhance combustion.

CONTROLS

The incineration system should be provided with a complete control system including a control cabinet with temperature indicator for each chamber and pilot lights for each component. The control system should perform the following:

Feeder Controls. Feeder start and stop controls with time for minimum load interval. Feeder operation should be precluded for maximum and minimum values of temperature.

Flame Safequard Controls. Controls should meet the requirements of IRI Insurance standards.

Burner Controls. Burner controls for the upper and lower burner chamber should be controlled for a maximum and minimum temperature.

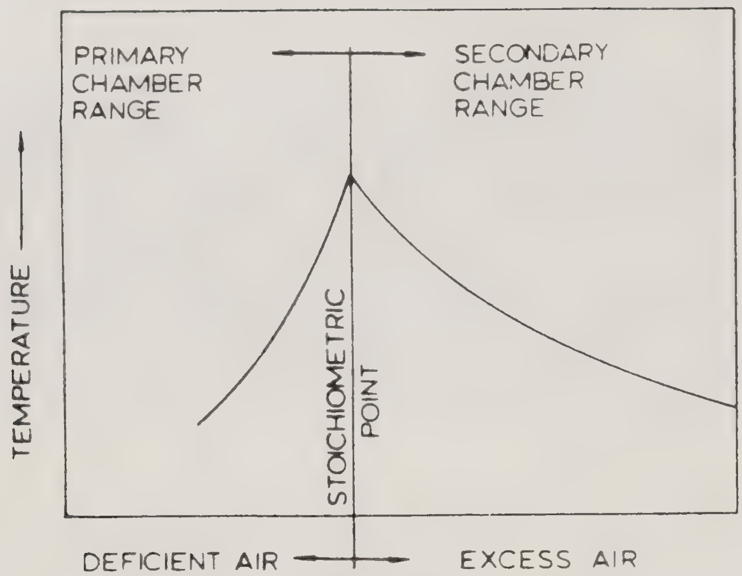
Automatic Adjustment. Automatic adjustment of fuel and air supplies should produce complete combustion of volatile gases and minimize harmful emissions. Automatic shutdown should be provided for cases of flame out, or fuel supply interruption. Burner for the secondary chamber should be continuously variable from full flow to 10% of full flow with automatic control for temperature.

Ash Removal. Controls for the ash removal system should preclude ash removal system operation when a receptacle is not correctly positioned to receive ash and when the receptacle is full.

Liquid Injection. Liquid injection controls should be interlocked with burner and loader controls to ensure conditions in the incinerator which allow complete combustion of the injected liquid.

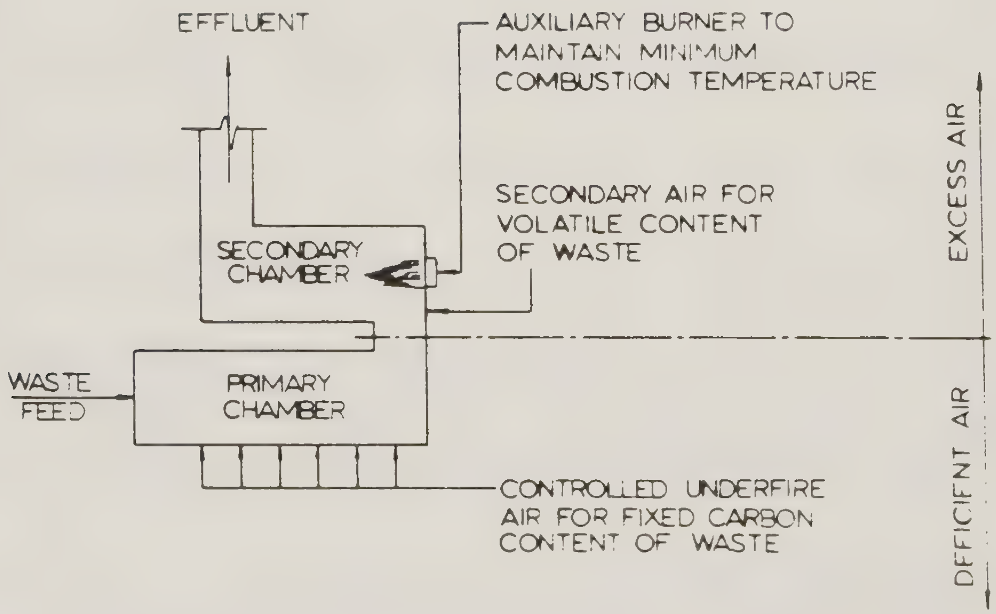
CONCLUSIONS

The amount and distribution of the total system air directly affect every key parameter on a controlled-air incinerator. A sound understanding of this air adjustment is the basis for optimum performance. Perhaps the second most important consideration is that of operator understanding of proper and consistent feeding. An incinerator reacts to thermal input. This thermal input is either furnished from the waste or from auxiliary fuel. Consistent feeding minimizes auxiliary fuel usage. Under these conditions the controlled-air incinerator has been and will continue to be one of the most satisfactory solutions for many kinds of waste disposal and especially so for hazardous wastes in general.



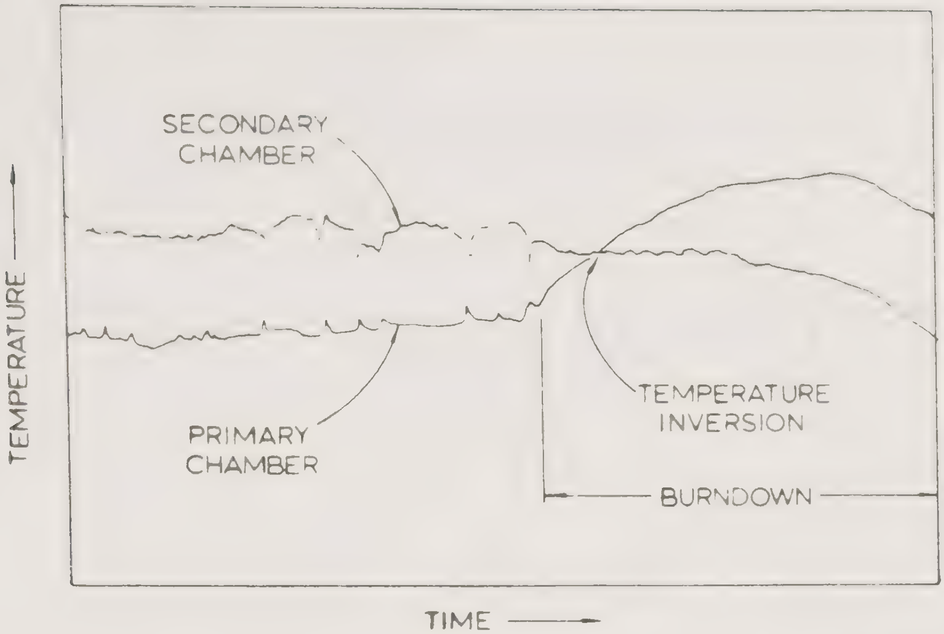
AIR AND TEMPERATURE PHILOSOPHY
FOR CONTROLLED-AIR INCINERATORS

Figure 1



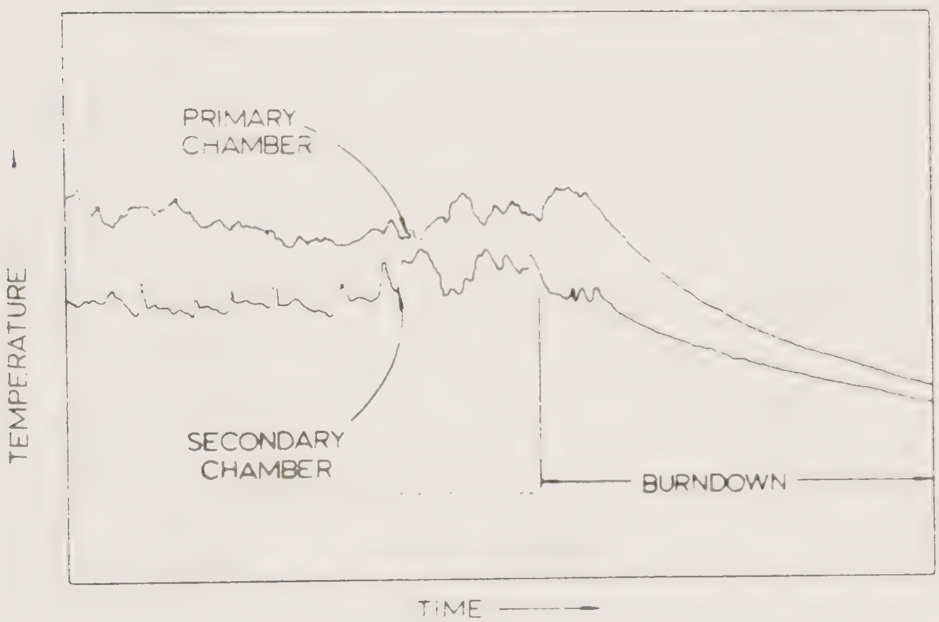
DESIGN PHILOSOPHY

Figure 2



TYPICAL TEMPERATURE PROFILE - VOLATILE WASTE

Figure 3

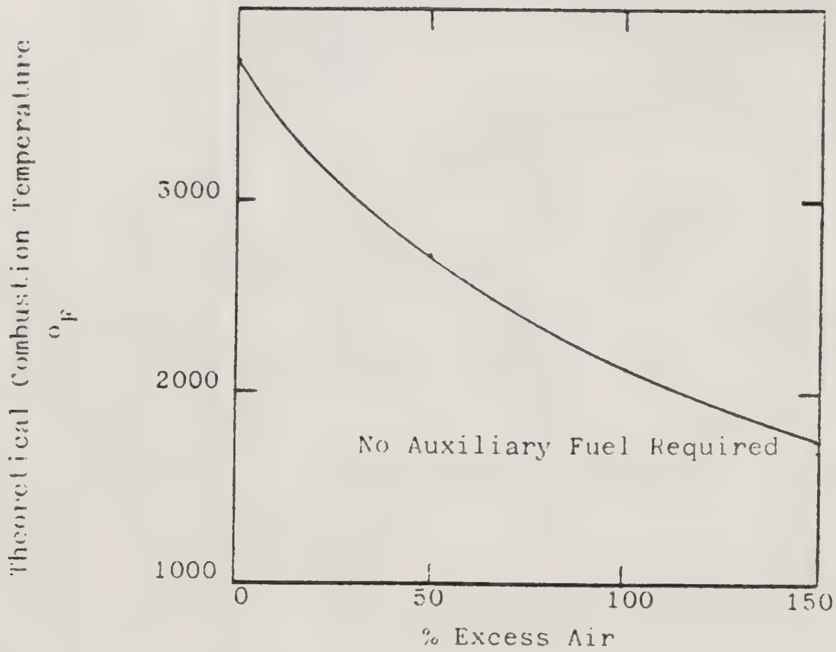


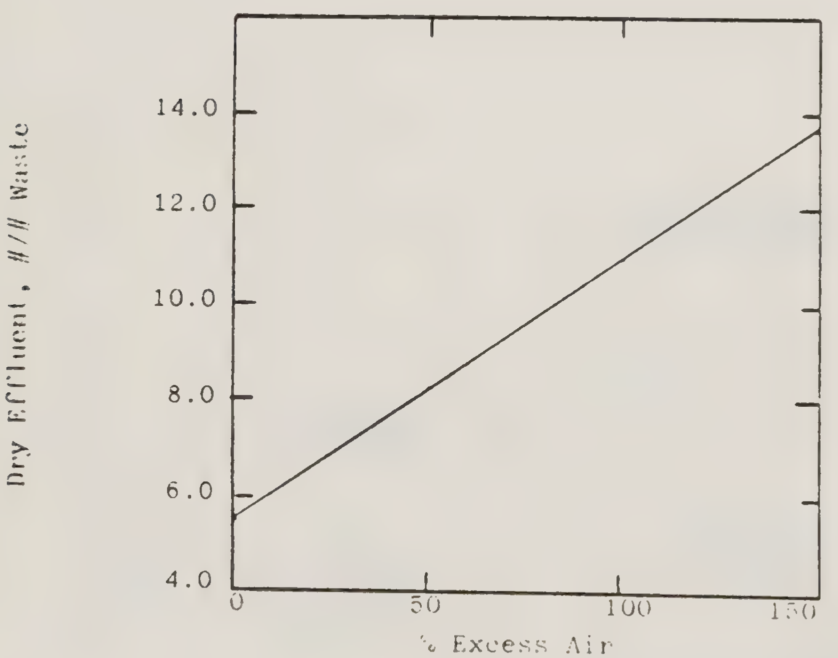
TYPICAL TEMPERATURE PROFILE - HIGH FIXED CARBON WASTE

Figure 4

Combustion Parameters

Type 0 Waste





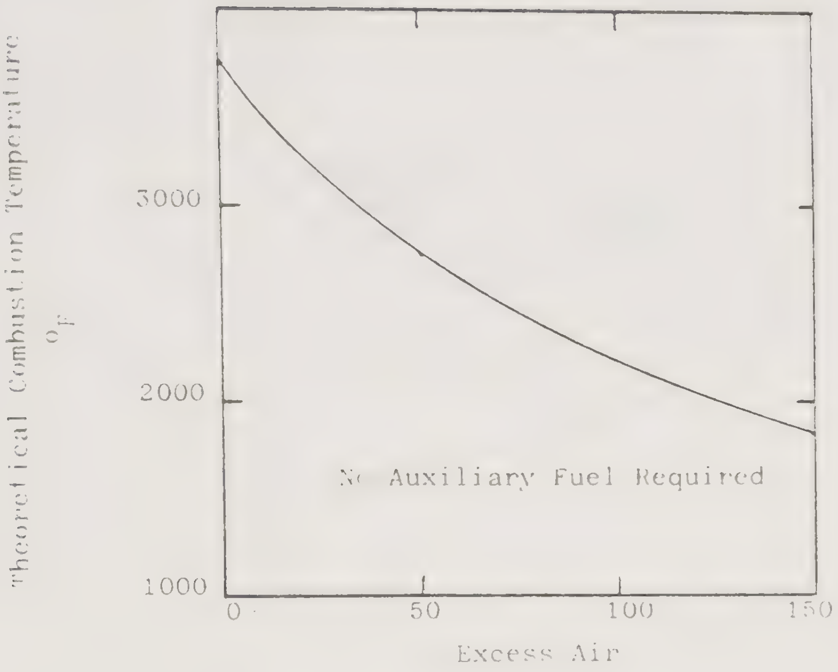
Formed Water From Waste = 0.519 # # Waste
Contained Water From Waste = 0.100 # # Waste

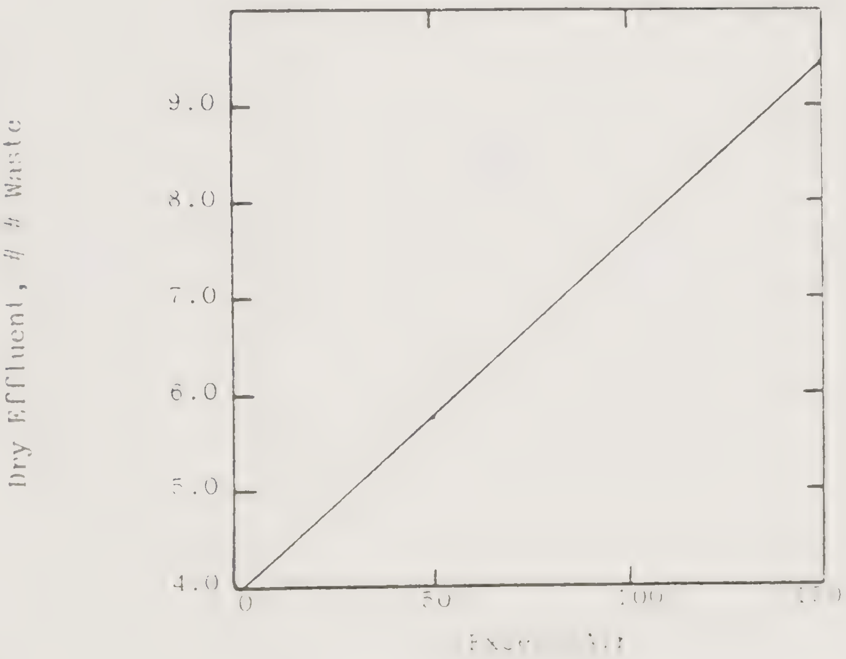
Total Water = 0.619 # # Waste

Figure 5

Combustion Parameters

Type 1 Waste





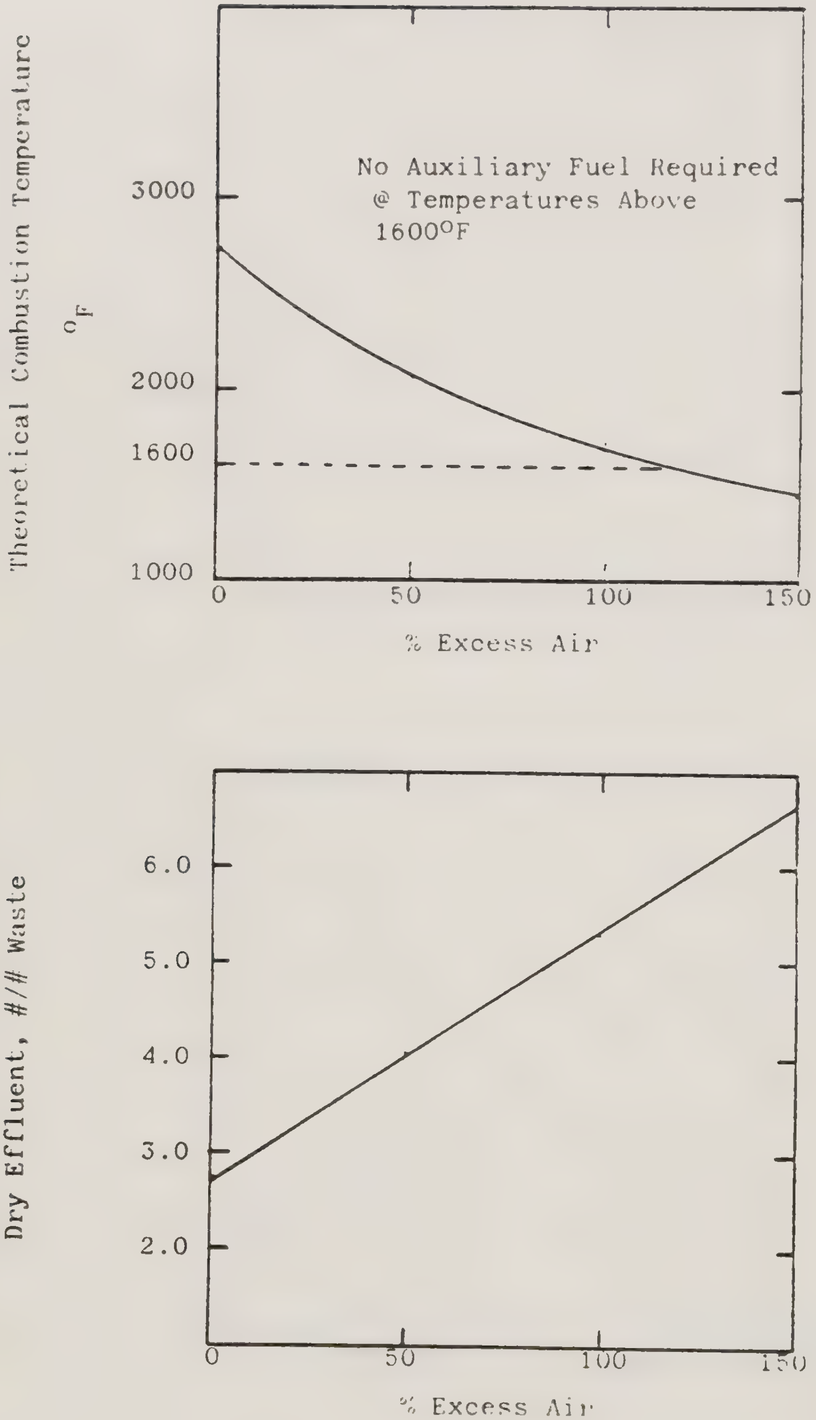
Formed Water From Waste = 0.348 #/# Waste
Contained Water From Waste = 0.250 #/# Waste

Total Water = 0.598 #/# Waste

Figure 6

Combustion Parameters

Type 2 Waste



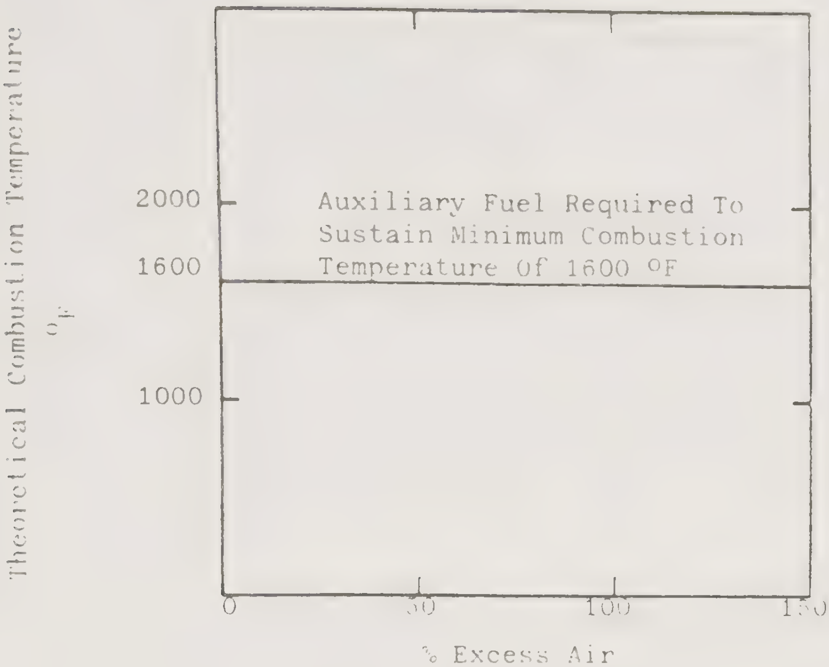
Formed Water From Waste = 0.232 #/# Waste
Contained Water From Waste = 0.500 #/# Waste

Total Water = 0.732 #/# Waste

Figure 7

Combustion Parameters

Type 3 Waste



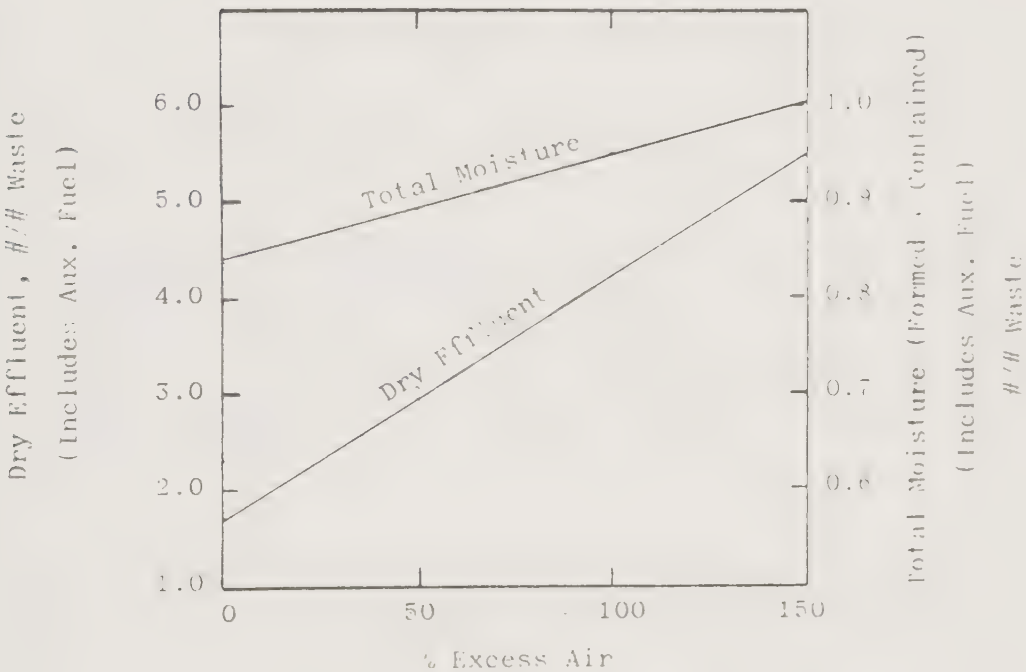
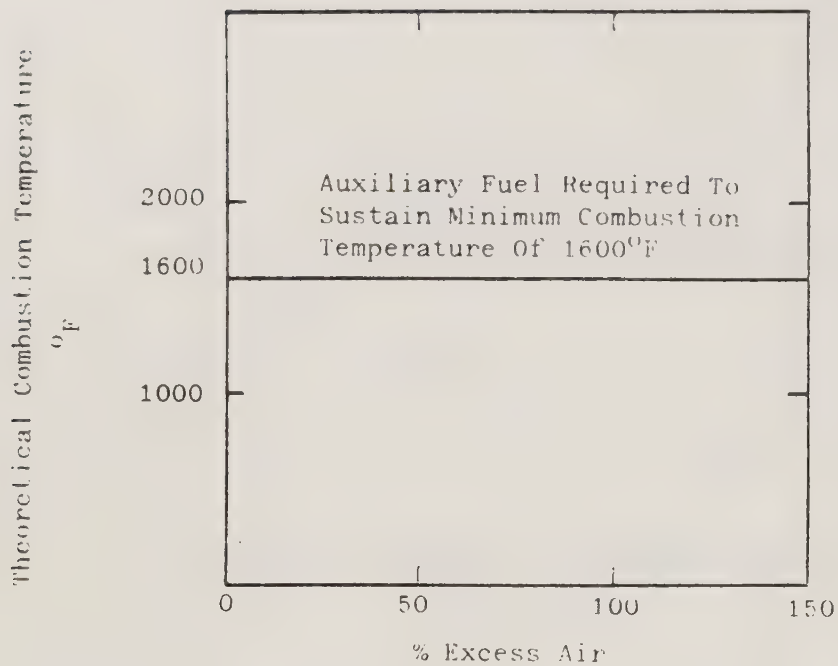


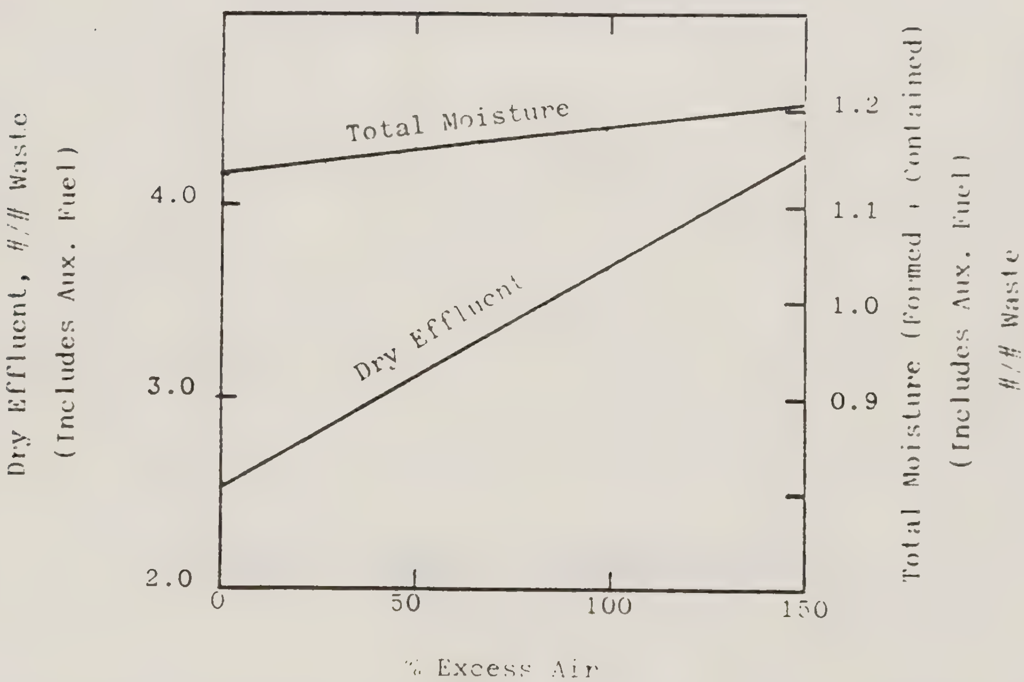
Figure 8

% Excess Air	0	50	100	150
Formed Water From Aux. Fuel	0.006	0.060	0.119	[illegible]
Formed Water From Waste	0.133	0.133	0.133	0.133
Contained Water From Waste	0.700	0.700	0.700	0.700
Total Water	0.839	0.893	[illegible]	[illegible]

Combustion Parameters

Type 4 Waste





% Excess Air	0	50	100	150
Formed Water From Aux. Fuel	0.200	0.226	0.249	0.275
Formed Water From Waste	0.081	0.081	0.081	0.081
Contained Water From Waste	0.850	0.850	0.850	0.850
Total Water	1.131	1.157	1.180	1.206

Figure 9

ENGINEERING ANALYSIS OF HAZARDOUS WASTE INCINERATION

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Introduction

The incineration of hazardous waste streams is a proven disposal technology. (1-3). Incineration and thermal destruction processes in general are ultimate disposal procedures which not only remove the hazard associated with the waste stream but also concentrate the residuals into much smaller volumes. At the present time, there is increased emphasis on thermal destruction of different types of waste streams due to

- the land fill ban on certain types of waste in the RCRA 1984 amendments
- the increased interest in thermal disposal treatment for material from superfund sites
- limited space and more restrictive design requirements for landfills

Waste generators, incinerator designers and regulatory agencies all face new challenges associated with the use of thermal destruction technology because of the need to burn a wide variety of new types of waste streams. The key issue facing them is to assure compatibility of the waste stream with the incineration system, i.e. to insure that the hazardous constituents can be effectively destroyed or removed.

The Energy and Environmental Research Corporation (EER) has developed an engineering procedure that can be used to remove some of the guess work from determining waste/destruction system compatibility. The methodology is a combined experimental and theoretical approach that builds on previous experience in fuel quality evaluations (4). In this paper will be presented an overview of the engineering analysis tools and the procedures used in evaluating the incinerability of waste streams.

Overall Approach

The key question is what is the correct thermal destruction system for a given waste stream in order to destroy the waste. Stated alternatively, is an existing facility capability of effectively treating a particular waste stream. In Figure 1 is shown the engineering analysis methodology for evaluation of waste stream incinerability. The waste stream is first characterized in sufficient detail (both physical and chemical) to specify the important properties affecting the incinerability of the waste. This is

followed by actual combustion testing of small quantities of the waste stream on process simulators. if the waste is pumpable then a liquid injection simulator is used; if the waste is solid a rotary kiln or fluidized bed simulator is used. These versatile process simulators provide detailed information concerning the technical requirements necessary to thermally destroy the waste. The final link to the system specification is a set of sophisticated computer models of the full scale processes. This engineering and system analysis step involves actual predictions on the performance of the full scale systems using the process simulator data as input. With this a prior prediction of performance, the risks associated with system design, construction and permitting can be minimized.

Process Simulators

EER is developing a complete set of hazardous waste test facilities which will allow the evaluation of waste streams and provide information on the conceptual designs of thermal destruction devices suitable to handle waste streams. Some of the test facilities are shown in Figure 2. The types of thermal devices that will eventually be simulated include the following:

- rotary kilns
- after burners
- fluidized beds
- liquid injection
- furnaces/boilers
- fixed hearths

These facilities will provide the capability of simulating the thermal treatment of materials in all conventional thermal destruction devices. Emerging thermal treatment technologies (e.g., infrared pyrsolysis, high temperature fluid wall,...) can also be examined by inference from the incinerability data or by relatively simple modifications of the existing facilities.

The thermal treatability of the specific waste stream can be examined by processing a relatively small sample (typically less than 100 lbs. of the waste) and testing in the simulator of interest. For each sample and each thermal technology the following information is determined:

- the fate of hazardous constituents in the particular waste stream for the thermal treatment technology
- combustion/thermal conditions required in order to obtain sufficient destruction efficiency

- special feeding, handling, and operating problems
- pretreatment requirements (dewatering, crushing,...)

The primary design variable of interest is the time/temperature history required to decontaminate the samples. This will be determined by systematically increasing the combustion temperature until complete decontamination is determined. The measurements made can include the following:

- Continuous on-line
  - HCN, $(CH)_2$, XN measured as total-N
  - H_2S, COS, CS_2, XS measured as total-S
  - HC's via total hydrocarbon (FID)
  - NO_x, CO, CO_2, O_2
- Discrete
  - GC/FID hydrocarbon species distribution
  - GC/NPD - CNspecies
  - GC/FPD - XS species
- Solid Residuals
  - Ultimate Analysis (C,H,N,S)
  - CN analysis (EPA standard method)
  - EP Toxicity

Engineering Analysis Computional Models

A large number of sophisticated computer codes are available which are applicable for engineering analysis of hazardous waste thermal destruction devices and experimental facilities. The computer codes originate from a wide variety of sources and are discussed in more detail elsewhere (5-8). Some of them are standard computational procedues frequently utilized by chemical engineering personnel that were developed many years ago. Others are specialized codes developed especially for the analysis of combustion data from research facilities which were refined over the years by EER. Still others are problem specific codes that were recently developed by EER for the EPA to analyze hazardous waste thermal destruction devices. In Table 1 is presented a summary of the computational models which are used as part of the engineering analysis methodology.

Scale Up Analysis

The purpose of this section is to demonstrate by means of a specific example, the type of procedures which are used to extrapolate the results from pilot scale studies to full scale applications. This section is based on work EER has recently completed for a private commercial client who is in the process of developing procurement specifications for a full scale rotary kiln to be installed in one of their plants in the Western United States. In this case the waste material was a relatively non-porous, low reactivity solid which could, in theory, be completely oxidized to inert, non-hazardous products.

The burning characteristics of the test material was investigated in the EER rotary kiln simulator. In the simulator, the fate of the components in the solid phase are directly followed by periodic solid sampling and continuous gas phase analysis. A batch of solids is loaded into the kiln and combusted for a predetermined residence time. The kiln exhaust was continuously monitored for O_2, CO, CO_2, NO_x and SO_2. In addition solid samples were periodically, withdrawn, from the bed and analyzed for the constituents. These measurements were used to indicate the extent of conversion of the test material.

The data shown in Figure 3a are typical oxygen measurements taken during a normal kiln test with fine sized test material (from 1/4 to 1/2 inch). As indicated, the oxygen flue gas droped initially and then began a slow ascent back to the baseline conditions. This decrease in flue gas oxygen is directly attributable to the combustion of the incinerable components in the waste. These experimental results were analyzed to yield instantaneous burning rates so that overall fractional convesion curves could be generated (see Figure 3b). The data are reported in terms of the percent of the initial charge which burned per hour as a function of time after charge introduction. The results shown in Figure 3b indicate that the burning rate rose rapidly as the charge heated up to the kiln temperature and subsequently decayed in a slow steady fashion.

A rotary kiln process model has been created as part of the hazardous waste incineration activities at EER to provide a methodology for comparing various experimental tests and to assist with the scale-up of the experimental results. Two separate computer programs were developed. The first model was designed to directly simulate the pilot scale kiln and is primarily used to derive the characteristic burning parameters for particular wastes. These parameters are adjusted so that the model can approxiamtely predict conversion, emission rate, and burning rate versus time data for the experiments conducted in the rotary kiln simulator. These parameters are then used in the second computer program to predict the axial conversion, temperature, emissions, and oxygen profiles in a full scale rotary kiln.

To generalize experimental results obtained in the pilot scale rotary kiln simulator, the second computer model was utilized. The mathematical concept involves dividing the kiln into multiple axial sections and the temperature and oxygen histories were assumed to be uniform across each section. The heat release from the auxiliary flame was allowed to occur in the first three zones according to an externally specified distribution. Heat transferred through the kiln wall by conduction and from the kiln exterior by radiation and convection were included. Axial heat transfer was neglected and the hazardous waste charge was assumed to burn at a temperature determined from the kiln wall temperature. In this manner the conceptual design of a kiln capable of adequately treating the waste stream can be defined.

Summary

The previous sections have described the process by which experimental data from the rotary kiln simulator are used in conjunction with computer modeling to predict the performance of a full scale unit. This particular example was somewhat unusual (and therefore particularly interesting) because the principal product of the hazardous waste oxidation was also a solid which remained in the kiln. The examples does, however, explicitly illustrate the steps required for translation of the experimental results into full scale predictions. A similar approach can be followed for other thermal treatment technologies using different simulators and theoretical analysis.

First, the parametric experimental studies in the rotary kiln simulator must be used to identify the physical processes which are controlling the hazardous waste destruction and to establish the influence of the key fundamental parameters (local oxygen concentration, solid and gas temperature, particle mixing, etc). These data are then used in conjunction with a computer model of the pilot scale kiln to derive the appropriate diffusion and kinetic coefficients. Once these coefficients have been properly validated by comparison with other experimental cases, they can then be included in the overall kiln model and full scale performance predictions can be completed with relative confidence.

Acknowledgment

The authors wish to acknowledge the continuing support of the U.S. Environmental Protection Agency and specifically to Dr. C.C. Lee who has provided significant guidance on the development of engineering analysis procedures.

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TABLE 1 ENGINEERING ANALYSIS MODELS

MODEL	CHARACTERISTICS
Furnace heat transfer code	Three dimensional heat transfer and combustion analysis for oil, gas and solid-fired furnaces, boilers, and incinerators
Energy and mass balance	Heat and mass balance for thermal destruction devices suitable for permit data evaluation
Incinerator performance code	Three-dimensional waste tracking and destruction code for incinerators
Coalescence-dispersion mixing submodel	Fuel-air mixing in prescribed incinerator flow field
Single droplet liquid injection submodel	Waste droplet trajectory, evaporation and destruction in defined flow field
Liquid injection spray flame submodel	Existing COM-3D turbulent spray code (three-dimensional) for liquid injection incinerator
General flame kinetics program	Versatile gas phase kinetics model for premixed flames with detailed flame kinetics

TABLE 1 ENGINEERING ANALYSIS MODELS (Continued)

MODEL	CHARACTERISTICS
General flame analysis program	Analysis code for gas phase premixed and diffusion flames with detailed flame kinetics
NASA equilibrium thermo dynamics program	Code for calculation of equilibrium concentration of species as function of temperature and stoichiometries
Elliptic turbulent flame code	Analysis of two-dimensional flame zones
Incinerator/furnace flow model	Three-dimensional analysis for flow patterns in thermal destruction
Incinerator risk analysis	Individual health risk assessment for simple incinerator/environment model
Jet mixing model	Trajectory, mass and momentum entrainment, and temperature of a circular ideal-gas jet in a prescribed crossflow
Electrostatic precipitator model	Electrostatic precipitator collection efficiency

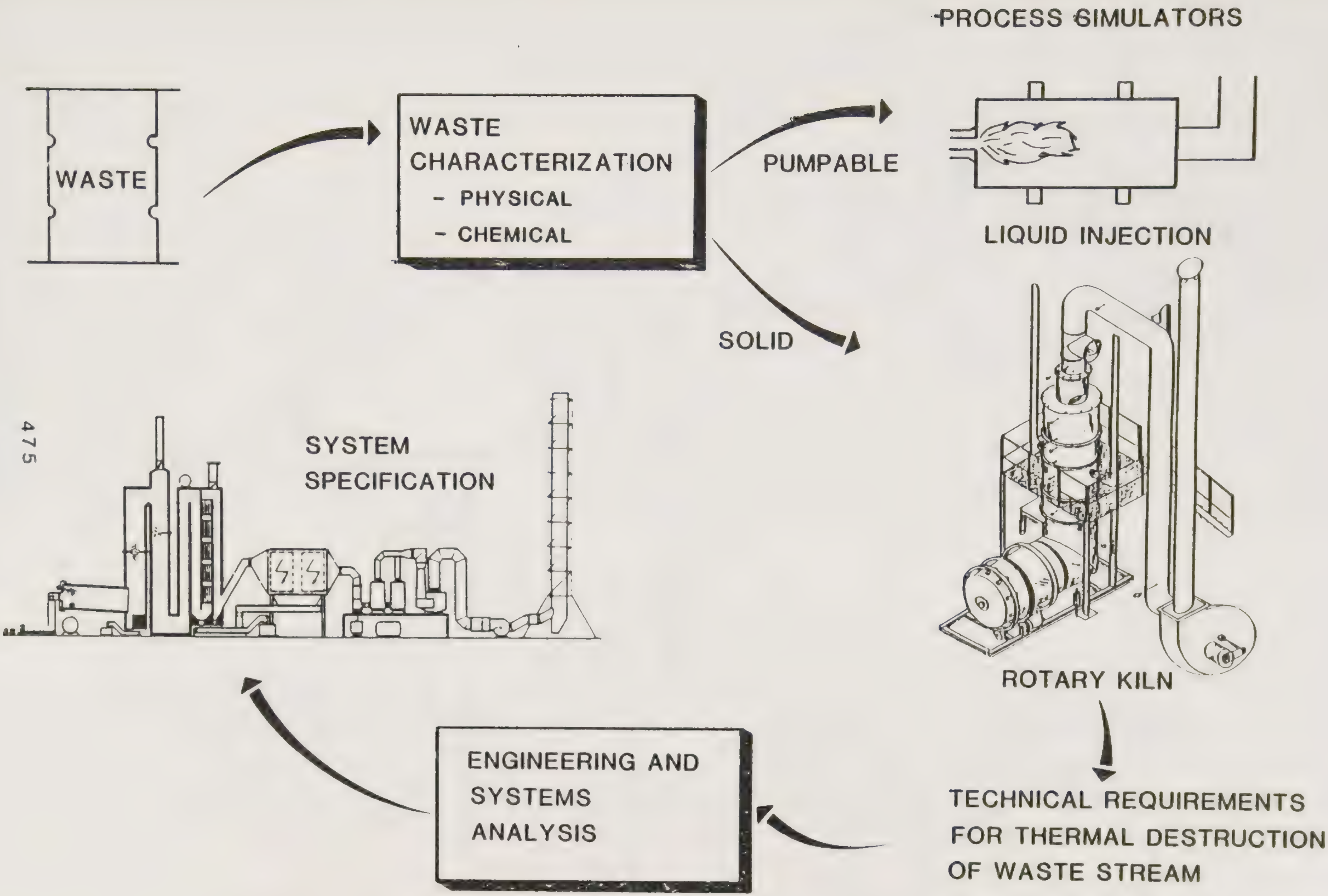

Figure 1. Engineering analysis procedures for specification of incinerator system for hazardous waste.

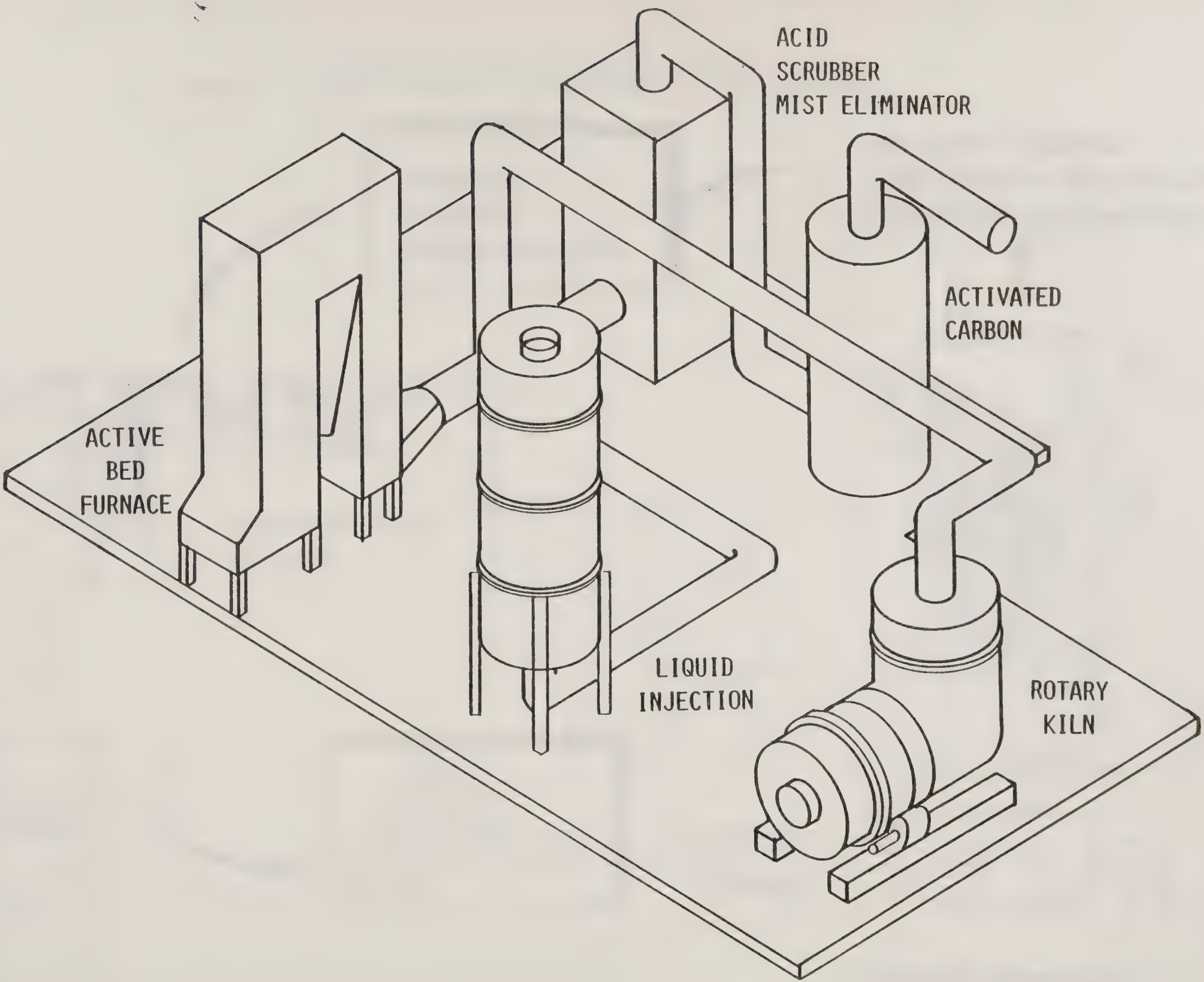

Figure 2. Hazardous waste test facilities.

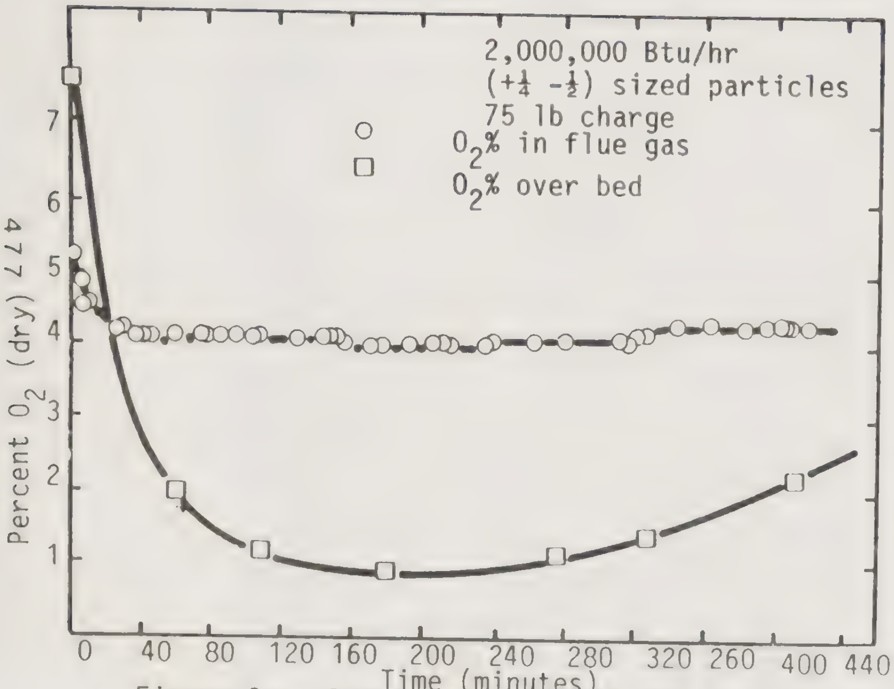

Figure 3a. Oxygen measurements for typical run.

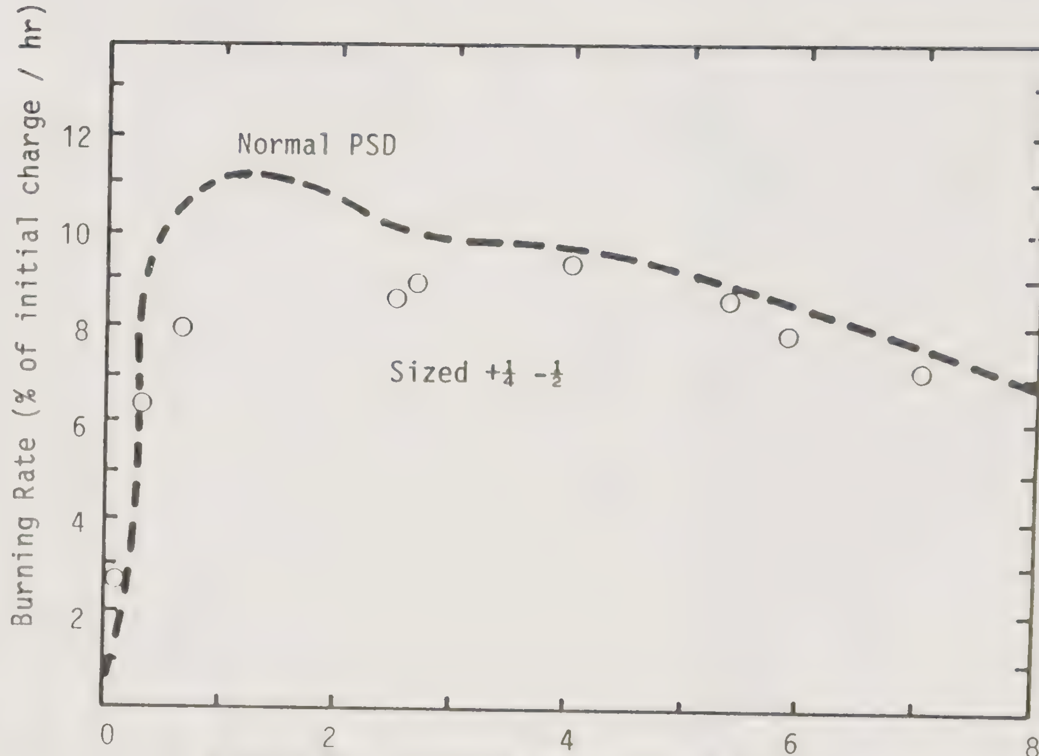

Figure 3b. Typical burning rate curve.

USE OF FREEZE CRYSTALLIZATION SYSTEMS FOR CONCENTRATION OF LIQUID HAZARDOUS WASTES

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BACKGROUND

Freeze crystallization is a separations process that works by converting selected components in a solution into pure crystals, and then separating them based upon their physical properties. The process is ideal for separating and concentrating liquid hazardous wastes prior to shipment, treatment or disposal. Freezing systems often work where other separations processes are not effective, for example, in applications involving aqueous organics or acids.

Much of the development work in freeze crystallization was performed for sea water desalting, with the objective of producing a drinkable product water having less than 500 mg/l of dissolved solids. A number of freeze systems were produced and successfully pilot tested for this purpose in the 1950 - 1980 timeframe, but were never commercially sold because other separations processes were found to produce drinking water as well and at less cost than freezing in this application.

In the past five years Heist Engineering has modified and extended freeze crystallization process systems to operate in a number of other applications where the cost and concentration efficiency of freezing compare more favorably with reverse osmosis, evaporation

and alternative separations processes. These applications typically involve organics, volatiles or materials that are corrosive at high temperatures, all of which are technically easier to separate with freezing. Further, the sizes of units required often are no larger than the pilot scale systems already proven for sea water desalting.

PROCESS DESCRIPTION

As shown by Figure 1, freeze systems involve three unit operations: freezing, separation and melting. Freezing takes place in a crystallizer: a vessel where the temperature and pressure are adjusted such that just the desired solution components change phase. Crystallizers are of various types, and use a variety of refrigeration cycles to remove heat. The type most suited to concentration of hazardous wastes uses a "secondary refrigerant", ie, a material that will vaporize at the temperature and pressure in the crystallizer, thereby drawing enough heat from the waste liquid to freeze some of it.

The frozen material is then removed from the crystallizer as a slurry and transfered to a second vessel to be separated from the remaining liquid. A gravity separation based on density variation is often the easiest and best to use, and can typically be accomplished in a wash column: a vessel where the frozen material is sprayed with water or another solvent and allowed to drain. The liquid, solid and refrigerant materials are then removed separately and either recycled or removed from the system. A number of wash column designs are available for use in hazardous waste applications.

After washing, the frozen material is melted and either reclaimed or discharged. Melters typically operate by reclaiming heat

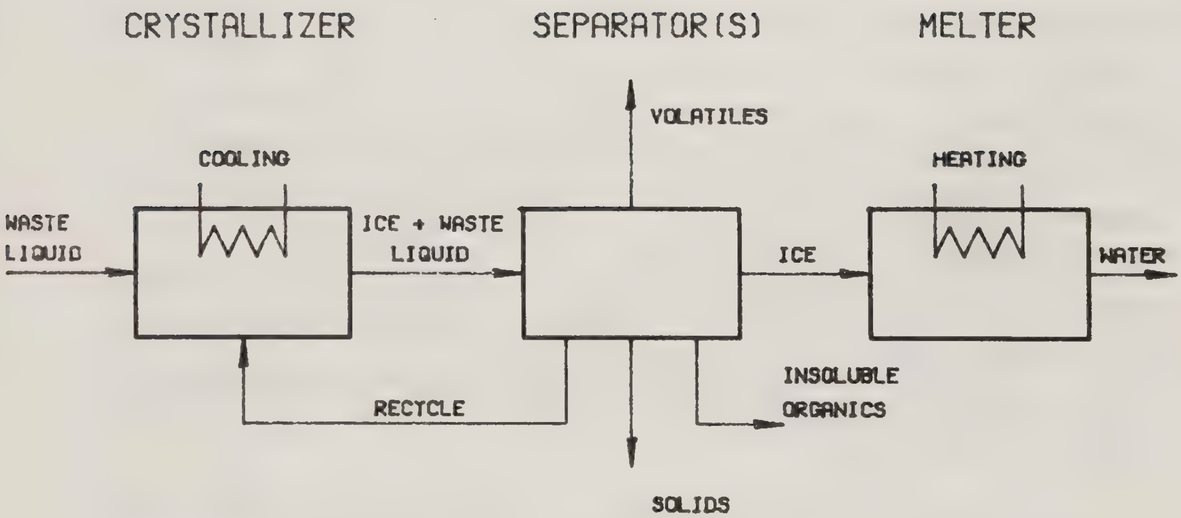

FIGURE 1 - FREEZE PROCESS STEPS

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rejected by the crystallizer refrigeration system. In fact, a number of energy loops of this type are built into the process to maximize its efficiency. It is typical for a secondary refrigerant process to require only 100 to 125 kWhr of electricity per 1000 gallons of liquid processed.

HAZARDOUS WASTE CONCENTRATION

Heist Engineering's secondary refrigerant process, Figure 2, can concentrate liquid wastes by a factor of as much as 20:1 to 30:1. This concentrating ability can be used to reduce the volume of material prior to transportation, incineration or disposal of the waste. Alternatively, the process can be operated to produce a concentrated chemical solution for reclamation and reuse. The water produced from the melted ice is usually sufficiently clean that it may be considered for discharge, or for on-site reuse. Contaminant removal efficiencies on the order of 1:10,000 or better are easily attained. This means that a 1.0% concentration of a contaminant in the feed stream is reduced to 1 ppm or less in the water effluent stream. As appropriate, a two-stage process may be used to further reduce the concentrations. The second stage can be either another freeze process or something different such as a carbon column. Also, pretreatment via a filter or oil-water separator will improve operations of the freeze system in some cases.

EQUIPMENT AND O&M COSTS

The total cost to build and operate a typical 5000 pound per hour (600 gph) secondary refrigerant freeze system is on the order of \$0.01 to \$0.04 per pound of liquid waste treated (\$0.10 to \$0.30 per gallon of waste), depending upon the application. Factors

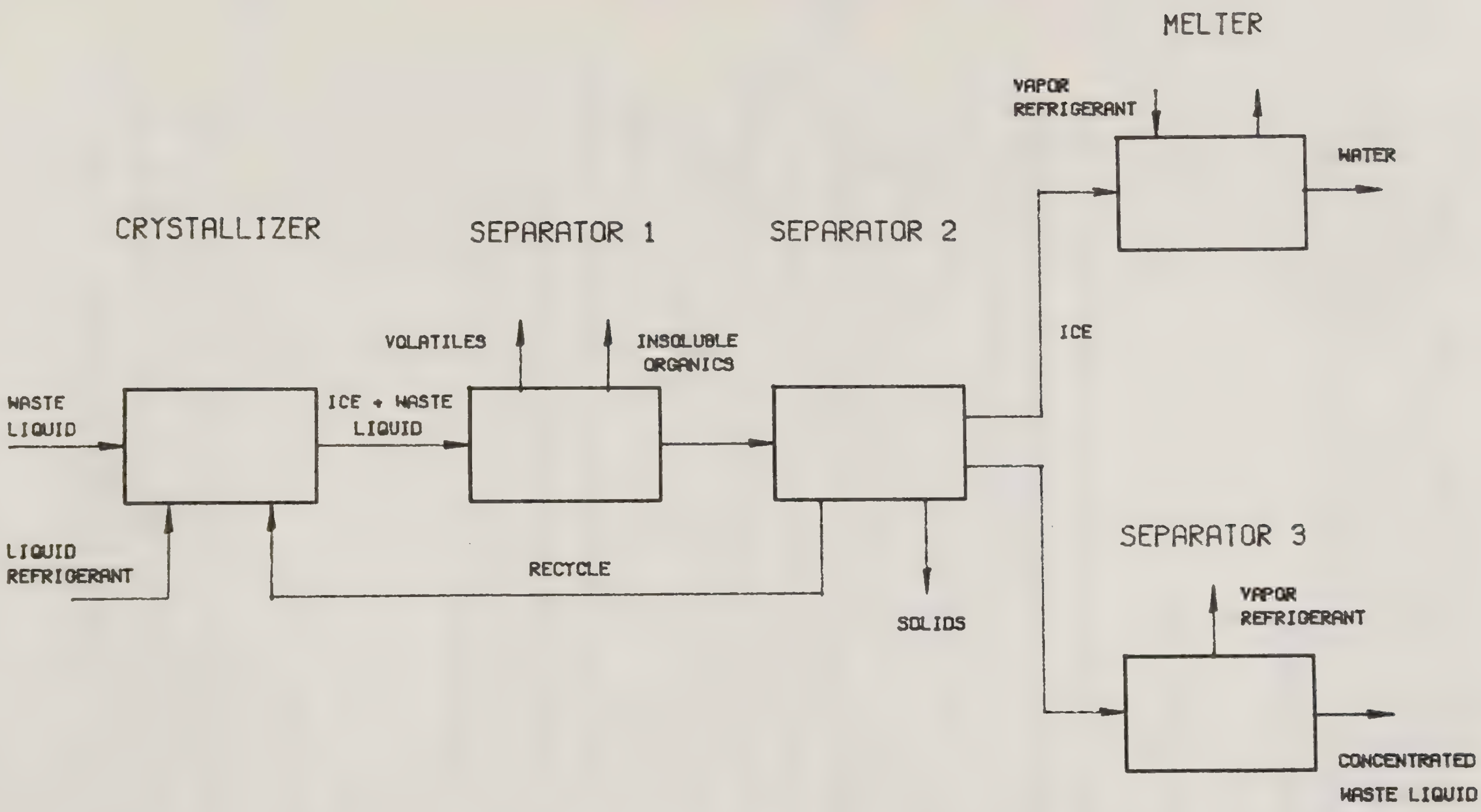

FIGURE 2 - SECONDARY REFRIGERANT PROCESS

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affecting cost include: corrosion potential, freezing temperature and liquid viscosity. Included in this total cost are equipment amortization (about 40%), electricity (5%), labor (35%), and maintenance costs (10%) for the freeze system itself. These costs include the major equipment and vessels, piping, fabrication materials and labor requirements for the freeze system. Costs for site development and other process systems are additional.

The return on investment (ROI) for use of a freeze system is determined by comparing the costs to build and operate other technically feasible alternatives. In one recent instance the next best alternative is hauling the liquid waste to a remote site for deep well injection at a cost of $0.40 per gallon. Here the use of freezing to pre-concentrate the transported waste has a ROI on the order of 55% to 60%. Where a valuable product is recovered the ROI can be significantly higher. In another recent application handled by five parallel freeze systems, there are two product recovery waste streams that have individual ROI's of over 100%, and the overall ROI for the five systems combined is about 75%.

TYPICAL HAZARDOUS WASTE APPLICATIONS

Three examples serve to illustrate the benefits to processing times and costs offered by Heist Engineering's freezing system.

1) Lagoon Remediation Heist Engineering's secondary refrigerant freezing process may be used to concentrate liquid wastes stored in lagoons or tanks. A portable (trailer-mounted) 5000 #/hr unit of this type is able to process 1 million gallons of waste liquid in just over two months of operating time. Costs are as discussed above. The forecast results of this processing on a representative project are:

920,000 gallons of dischargable water;

80,000 gallons of waste brine; and

150,000 pounds of waste salts.

2) Incinerator Pre-Concentration The secondary refrigerant process may be also used with an existing incinerator to increase the amount of waste that can be processed in a given time period, or may be used to process the same flow of wastes but at a lower firing rate. For example, the capacity of a small 1 mmBtu/hr portable system can be increased from 250 #/hr to 5000 #/hr of liquid waste feed. The system can then process 1 million gallons of waste in 2 months compared to the former time of over 40 months. The unit cost for this processing reduces from $0.20 per pound ($1.60 per gallon), for the incinerator operating alone, to somewhere in the range of $0.04 per pound ($0.30 per gallon), for the freezer and incinerator operating together. The products of this processing are:

920,000 gallons of dischargable water;

2,500,000 pounds of exhaust (mostly air & water);

110,000 pounds of waste ash; and

150,000 pounds of waste salts.

2) Acid Waste Reclamation The secondary refrigerant process is uniquely suited to the concentration of waste acids such as those from steel pickling, metal finishing and ore processing. In some of these applications it is possible to recover reusable salts as well. Vessels, equipment and piping are protected in response to the corrosive environment in which

these freeze systems operate, increasing the fabrication costs by about one-third. The desired product acid concentration may require a somewhat larger than usual refrigeration system as well, further increasing both the fabrication and energy costs. A 5000 #/hr plant of this type therefore costs on the order of $0.04 per pound ($0.30 per gallon) of waste liquor processed. The value of reclaimed chemicals significantly reduces this cost of owning and operating the plant.

CONCLUSIONS

The freeze process should be considered for separating and concentrating those liquid hazardous wastes where alternative technologies either do not work, or cost more to own and operate than about $0.10 per gallon.

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Heist Engineering has published the following overview technical papers having to do with freeze processes and several applications that Heist has evaluated for their use.

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MEDICAL SURVEILLANCE:
A MUST IN THE MANAGEMENT OF HAZARDOUS MATERIALS

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INTRODUCTION

The recent identification of hazardous waste sites across the United States and the demand for their prompt clean-up has resulted in the creation of a new industry in this country, with its own unique class of workers. Unlike the tradional occupational setting, where workers are exposed to a relatively stable physical and chemical environment, hazadous waste workers often deal with large quantities of unknown chemicals under diverse and challenging conditions. In addition, while most industries rely on engineering controls to reduce worker exposures, hazardous waste workers must depend largely on the use of personal protective equipment. These distinctions, and the widespread concern over potential short and long term health effects of exposure hazardous waste, challenge the occupational physician in the development of adequate program to assess worker health.

BASELINE EVALUATION

Preplacement Evaluation

The use of pre-placement medical examinations to assess employee fitness is particularly relevant to hazardous waste workers. The examining physician needs to consider not only the physical demands of the work itself, but also the physical demands associated with the extensive use of personal protective equipment. The use of confining garments and gloves may result in heat stress and skin irritation. The use of respirators, particularly non-powered, air filtering masks, will place an increased demand on the heart and lungs, especially during the performance of manual labor.

These physical demands, in a potentially dangerous environment, justify the use of rigorous selection criteria.

During the clean-up of a site there is always the possibility of a major accident or emergency. Persons with medical conditions which are associated with sudden decompensation or collapse should be precluded from regular job duties where evacuation or emergency response efforts may be required. These would include conditions such as seizure disorders or insulin-dependent diabetes, along with severe or poorly controlled heart and lung diseases. Persons with underlying disorders of the liver, kidney or blood system may be at increased risk of injury due to acute high dose or chronic low level exposure and should also be precluded from regular duties which carry a high risk of exposure. Figure 1 lists the conditions which are relative contraindications for hazardous waste work. The decision to restrict an individual will vary, depending on the severity of the condition and the individual's specific job requirements.

Establishment of Employee Baseline Values

In addition to assisting in proper worker selection and placement, medical examinations will provide a baseline for subsequent evaluations. The baseline examination will need to be relatively comprehensive to include the health parameters which may later need to be evaluated. Figure 2 lists an example of a baseline evaluation of hazardous waste workers. This is similar to the standard medical examinations used in other industries. The medical questionnaire will aid the examining physician in the detection of the conditions which may require work restriction. The questionnaire should also include symptoms. Changes in worker symptomatology may occur before actual physiologic changes become apparent and may serve as a means of early detection of adverse health effects. The physical examination will provide the physician an opportunity to the review the questionnaire with the worker. The physical examination will also allow the physician to detect conditions which were not reported by the worker and which may impact job performance. Baseline assessment of the skin and the nervous system are best accomplished by physical examination.

Laboratory testing should be used to assess liver and kidney function and the integrity of the blood forming elements in the bone marrow. Evaluation of lung function should include spirometric measurement of pulmonary function and a chest x-ray. Cardiovascular evaluation should include an electrocardiogram. Exercise testing should be considered in employees with highly physical job requirements, after the age of forty. Workers with abnormalities detected on the baseline examinations will need to have further evaluation by their personal physicians. Whether an underlying

condition or abnormality will result in a job restriction will depend, again, on the nature of the finding and the job description. The ability to rely on these tests as an indication of possible health effects due to worker exposure requires the documentation of normal baseline values.

The measurement of chemical substances in blood, urine, hair or fat will establish baseline levels for subsequent comparison. Figure 3 lists some of the more common substances which have been measured in hazardous waste workers along with with the most suitable biological media. The utility these measurements in monitoring the health of workers is limitted by the accuracy of the detection method and the biological half-life of the material in the body. The choice of the persons, timing and methods of the sampling will depend on the individual project.

MEDICAL SURVEILLANCE

Purpose

A medical surveillance program can serve several functions in assuring the overall health and safety of hazardous waste workers. A comprehensive pre-placement examination guarantees that the workers are physically able to perform the work without unnecessary risk to themselves or to others. Selected use of physiologic testing or biological monitoring will confirm the effectiveness of personal protective equipment and other safety measures in preventing employee exposure. A comprehensive program emphasizes to workers the importance of strict compliance with safety standards and confirms the company's commitment to worker health.

Periodic Examinations

The selection of the appropriate content and time interval for periodic medical examinations will depend on the nature of a clean-up activities. Workers required to spend several months at a single site should have periodic measurement of laboratory tests shortly after the project has begun, particularly if accurate characterization of the chemicals present at the site has been delayed. Workers with the highest risk for exposure should have complete examinations after each major project. More peripheral workers, such as laboratory technicians and engineers, or those who work at various different sites should receive complete examinations yearly, with laboratory testing at more frequent intervals depending on degree of potential exposure. The use of appropriate biological monitoring will aid in the interpretation of the laboratory tests in the individual worker, particularly if an abnormality is detected

that is associated with an chemical known to have been present at the site.

Epidemiologic Studies

Even in relatively small companies, epidemiologic methods may be applied to the information obtained in the periodic medical evaluations. This approach can further enhance the ability to detect subtle health effects if they are present. Selected high risk workers can be analyzed as a group to look for clusterings of symptoms, abnormal findings or trends. Findings can be correlated with industrial hygiene and biological monitoring data. Employees with less exposure may serve as internal control groups in these surveys. The use of computers to store the results of the medical examinations greatly facillitates this type of analysis. Programs can be designed for both cross-sectional and longitudinal analyses and to record individual and site-specific exposure data. This approach allows for presentation of the results of medical surveillance in the occupational health literature to document and advance the effectiveness of health and safety efforts in this industry.

CHRONIC HEALTH EFFECTS

Two of the major concerns of workers in this industry involve the risk of adverse reproductive effects and cancer. Certainly, these are the two problems which received the greatest attention in communities surrounding hazardous waste sites. While ongoing surveillance activities may address the efficacy of work practices in preventing the development of demonstrable physiologic abnormalities, the possibility that workers are being continuously exposed to low levels of hazardous chemicals remains. Demonstration of the presence or absence of these effects requires carefully controlled study of a large number of workers. This will require cooperation with efforts to follow workers in this industry over the ensuing years. Ultimately the study of these workers may serve greatly in aiding our understanding of these issues for the general public.

FUTURE CONSIDERATIONS

The availability of tests which can accurately characterize exposure to genotoxic substances may soon be applicable to the surveillance of hazardous waste workers. While the relevance of these tests to the development of disease is uncertain, they may

provide a more accurate measure of the adequacy of personal protective equipment. In addition, certain tests are able to detect chronic low level effects which may more accurately relate to actual worker exposure. Other investigative tools, such as neurophysiologic and neuropsychological testing are not yet applicable to this occupational setting.

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FIGURE 1.

Relative Contraindications to Hazardous Waste Work

Significant Respiratory Disease
Significant Cardiovascular Disease Liver Disease
Kidney Disease
Hematologic Disorders
Chronic Skin Disorders
Insulin-dependent Diabetes
Seizure Disorders
Psychiatric Disorders

FIGURE 2.

Medical Examination for Hazadous Waste Workers

- Medical Questionnaire
- Physical Examination
- Laboratory Testing
    - Complete Blood Count
    - Liver Enzymes
    - BUN/Creatinine
    - Urinalysis
- Pulmonary Function Testing
- Chest X-Ray
- Electrocardiogram
- Exercise Treadmill Test
- Biological Monitoring

FIGURE 3.

Biological Monitoring for Hazardous Waste Workers

Substance	Medium
Lead	Blood
Arsenic	Urine, Hair
Mercury	Blood, Urine
Cadmium	Blood, Urine
DDT	Blood, Fat
Lindane	Blood
PCB's	Blood, Fat
Hexachlorobenzene	Blood, Fat

OLFACTORY INJURY AND ODOR ANNOYANCE DUE TO CHEMICAL EXPOSURES

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Vulnerability of the Sense of Smell

The sense of smell arises from two patches of nervous tissue, in the uppermost clefts of the nasal cavities. Presumably functioning in Nature to monitor our air and food for any potentially harmful scents or spoilage, the sense of smell is also likely to be the first tissue at risk from inhaling possibly toxic industrial vapors, fumes and dusts. Nevertheless, the sense of smell is also susceptible to other negative influences, such as infections, drugs and injuries. It is necessary to establish a clear picture of the normal performance of the human sense of smell, and how it varies as between different individuals in the population, before one can form an opinion as to whether a given industrial chemical exposure could have been responsible for damage to this important organ.

If the sense of smell has been completely lost, this can be established by the examining physician with rather informal tests, using coffee-grounds, a cigarette-butt, etc. to test the patient's responses. Nevertheless, in the more usual situation, there is only a partial, or suspected, decrease of sensitivity. To establish this requires quantitative measurements of the odor thresholds of comparable groups of workers, evenly matched except for their differing exposure to the suspect chemical. The odor threshold is the lowest concentration of a chemical in air that 50% of the people tested can reliably distinguish from clean air.

Supposing the average threshold for a group of similarly-exposed workers is significantly different from that of a non-exposed group, then chemical damage to the sense of smell may be suspected. A reduction of smell sensitivity, typically below one-sixteenth of the average normal sensitivity, is considered a hyposmia. True anosmia means a lack of any olfactory sense at all, but a reduction of sensitivity to 1/250th. of the normal mean may be taken for all practical purposes to be anosmia.

Hyposmia and Anosmia Due to Chemical Exposure

The data to be summarized in this paper are taken from a worldwide literature search by Amoore (1), published this year, in which cases of hyposmia due to chemical exposure in the workplace were reviewed. Wherever possible, any quantitative odor thresholds were converted to common units of binary steps deficiency (each binary step represents a doubling of the threshold concentration for the test chemical, or a halving of the smell sensitivity). The mean threshold sensitivities and frequencies of occurrence of the exposed, and control, groups of workers were then compared, to evaluate the chemically-induced deficiency.

Although there is some overlapping, it is helpful to classify the chemically induced hyposmias according to how rapidly or slowly the damage was done, and how long the injury persisted:

Exposure	Hyposmia	Duration	Examples
ACUTE (sec/min/hrs)	Temporary	minutes	H_2S HCN
	Recuperable	weeks	H_2Se $ZnSO_4$
	Permanent	years	$POCl_3$ SO_2
CHRONIC (months/years)	Recuperable	weeks	Acetone
	Permanent	years	$ZnCrO_4$ Cl_2

At one end of the scale, a single inhalation of fumes containing sulfur dioxide has been reported to cause a permanent loss of the sense of smell. This anosmia is clearly an acute injury. On the other hand, exposure to the dust of cadmium oxide over several years can lead to a permanent anosmia, which in this case is a chronic condition.

There are many examples of olfactory damage due to chemical fumes and vapors. All the data have been assembled into eight Tables in the cited Review (1). The reports are classified according to the chemical class of the substances considered responsible for causing permanent hyposmia in man. These include examples of metallurgical processes, metallic compounds, dusts, non-metallic inorganics, organic compounds, and miscellaneous manufacturing processes. The facts that some very common industrial materials are suspected of causing hyposmia and that the damage may even occur at or only slightly above the recommended permissible exposure limit, suggest that evaluations of industrial hygiene should also take into account possible injury to the sense of smell.

Annual Testing for Olfactory Sensitivity?

An intact and functional sense of smell is an important safeguard for workers exposed to potentially injurious or dangerous chemicals. The nose can be an indicator of over-exposure to regulated substances, or even help to detect a leak or other equipment malfunction. A worker who has suffered olfactory damage on the job is not only more unsafe

around chemicals, but also has lost a faculty that is essential for full enjoyment of flavors and perfumes. As such he or she may be entitled to compensation or disability. Although the AMA guidelines recommend only a 3% disability for permanent bilateral anosmia, much larger disabilities have been recommended by West German authorities (1), rising to 100% for any worker who depends professionally on his sense of smell, such as a head chef or tobacco blender.

In these circumstances it would be prudent to institute annual olfactometric testing of any workers who are exposed, or may be exposed, to chemical vapors and dusts. This is by analogy with the annual audiometric testing for workers in noisy environments. In this way, early damage to the sense of smell could be detected while recovery may still be possible, and operational procedures can be changed to decrease the workers' exposure.

The Problems of Odor Annoyance

Less extreme than olfactory injury, but also potentially highly damaging to industrial interests, is the common occurrence of "odor pollution". In many industrial processes, it is well-nigh impossible to prevent some odorous gases or vapors from escaping out of the plant and drifting over the factory boundaries toward neighboring industrial, commercial or residential areas. Although the vapors may be of such a nature, and at such low concentrations, that they are most unlikely to cause medical symptoms of injury, nevertheless an unwanted smell may be considered legally a nuisance, and can easily produce physiological and psychological problems for neighbors who are exposed.

At the request of the California Air Resources Board a study was recently completed on the evaluation of odor annoyance due to hydrogen sulfide (2). Among several published sources that have attempted to evaluate odor annoyance scientifically, the most informative was that by Winneke and Kastka (3). They studied the odor intensities (dilution-to-threshold ratios) at various distances down-wind from an insulation plant (phenolic odors) and a tar-oil plant (hydrocarbons and sulfur compounds). They also developed a comprehensive questionnaire for evaluating the degree of annoyance caused by the odors to the residents near the factories. Forty possible odor-annoyance reactions were rated on a scale from 0 to 6 for degree of annoyance. These included generalized annoyance due to the odor sensation itself, social annoyance affecting everyday life, and somatic annoyance, actually believed to cause headaches or nausea.

From the results obtained by these and other authors, Amoore (2) concluded provisionally that the average threshold of odor annoyance, for various unpleasant odors, occurs at about 5 times higher concentration of odorous substance in the air than the average threshold of odor detection for the same substance. That is to say, when an unpleasant odor reaches a concentration 5 times that at which 50% of the population can detect the odor, then 50% of the exposed population will complain of at least occasional headache, nausea or other symptoms that they ascribe to the odor.

Of course, downwind odor pollution is unlikely to be constant, but varies according to irregular release rate and fluctuating wind. Also, people living in a mildly odorous environment are likely to develop an adaptation or "odor fatigue" so that they do not notice a low background level of odor. Nevertheless, the methods of data collection employed by Winneke and Kastka (3) appear to compensate for the variables of pollution concentration and odor fatigue, so that the estimated 5-fold factor between odor threshold and odor annoyance represents a realistic assessment.

Recent Complaints over Industrial Odors

In California the principal population centers have Air Quality Management Districts (AQMD) that are usually the first point at which specific odor complaints from the public are received concerning a particular business facility, such as refuse transfer or automobile painting. In cases involving a more widespread problem, such as hydrogen sulfide that can arise from various industries including sewage treatment, petroleum refining, pulp mills and geothermal operations, the California Air Resources Board aims to maintain a Statewide policy (2). Where residents in a neighborhood feel very strongly that their wellbeing and/or health has been adversely affected, for example by ammonia odor from agricultural fertilizer, or by odors from sewage treatment, then a suit may be brought to seek relief. Substantial settlements or judgments have been known to result from such actions.

In most cases of which our Firms are aware, the official assessment of odor strength has been made by Inspectors or other evaluators whose personal olfactory sensitivities are unknown, and who have not used any objective standards of odor intensity or dilution-to-threshold ratio in reaching their opinions. In fairness to all parties of the disputes, and considering that the comfort of hundreds of residents as well as millions of dollars of industrial investment may be at stake, we appeal for the development and adoption of scientifically valid odor threshold and annoyance criteria in the State of California.

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CHEMICAL SPILL RESPONSE

IN

CLEAN ROOMS AND LABORATORIES

by

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Chemical spills present special hazards to employees and to persons assigned to clean-up the spill. Every effort must be made to protect all persons from the particular situation presented by the "chemical out of control". In some situations, however, the spill response procedures may cause significant damage and disruption to the work place. Semiconductor clean rooms are the most obvious location in which dust and dirt introduced by the clean-up can cause significant problems. However, other locations, such as R & D laboratories, quality assurance laboratories, computer rooms, and photographic dark rooms also are vulnerable to excessive damage caused by clean-up procedures.

As the management of chemical spills has increasingly become of interest to American companies (read that "as American companies are increasingly willing to spend money on spill prevention and response"), many new products have been introduced to help cope with spills. While all such products are claimed by their manufacturer as the best stuff for spills since mops, each product has its advantages and its limitations. Failure to understand either can lead to ineffective clean-up or to injury of personnel.

During the past several years Chemical Safety Associates, Inc. has been working on improving the procedures for spill management, including training spill teams, and evaluating spill clean-up products. In this paper, and during the accompanying demonstrations (Tuesday and Thursday - noon) we will describe the procedures and demonstrate the materials now recommended.

CHEMICAL SPILL RESPONSE PROCEDURES

A spilled chemical is defined as a "chemical out of control". In general, we assign some minimum level, below which, area workers and area supervisors can clean-up the spill themselves. Over that amount requires notification of the plant emergency team. Operationally, we have found the amount to vary from 1 liter to several gallons. In "clean" areas, the 1 liter level is most appropriate.

The essential concern during any emergency, including a chemical spill, is the PROTECTION OF HUMAN HEALTH and SAFETY. In so far as this principle is not violated, we attempt to protect the facility and the environment. When a spill occurs, it is the responsibility of those immediately involved to respond in such a manner which will minimize the threat to their health and safety and will also obtain help. The chart on the next page represents a generic spill response matrix used as a starting point for preparing and implementing customized spill plans. Each employee must understand that they are expected to

CLEAR THE AFFECTED AREA
CONTACT EMERGENCY
CHECK FOR PERSONAL INVOLVEMENT

A risk assessment must be performed for every spill. Spills such as oil, hydraulic fluid, etc, outside clean environments, should be cleaned up by area workers, supervised by a member of the spill team. High risk spills MUST be handled by trained spill response personnel.

Following the high risk path on the chart outlines the procedure. In general, at least EPA LEVEL B protection is used, until the hazard has been sufficiently controlled to use air purifying respirators and finally, regular work clothes.

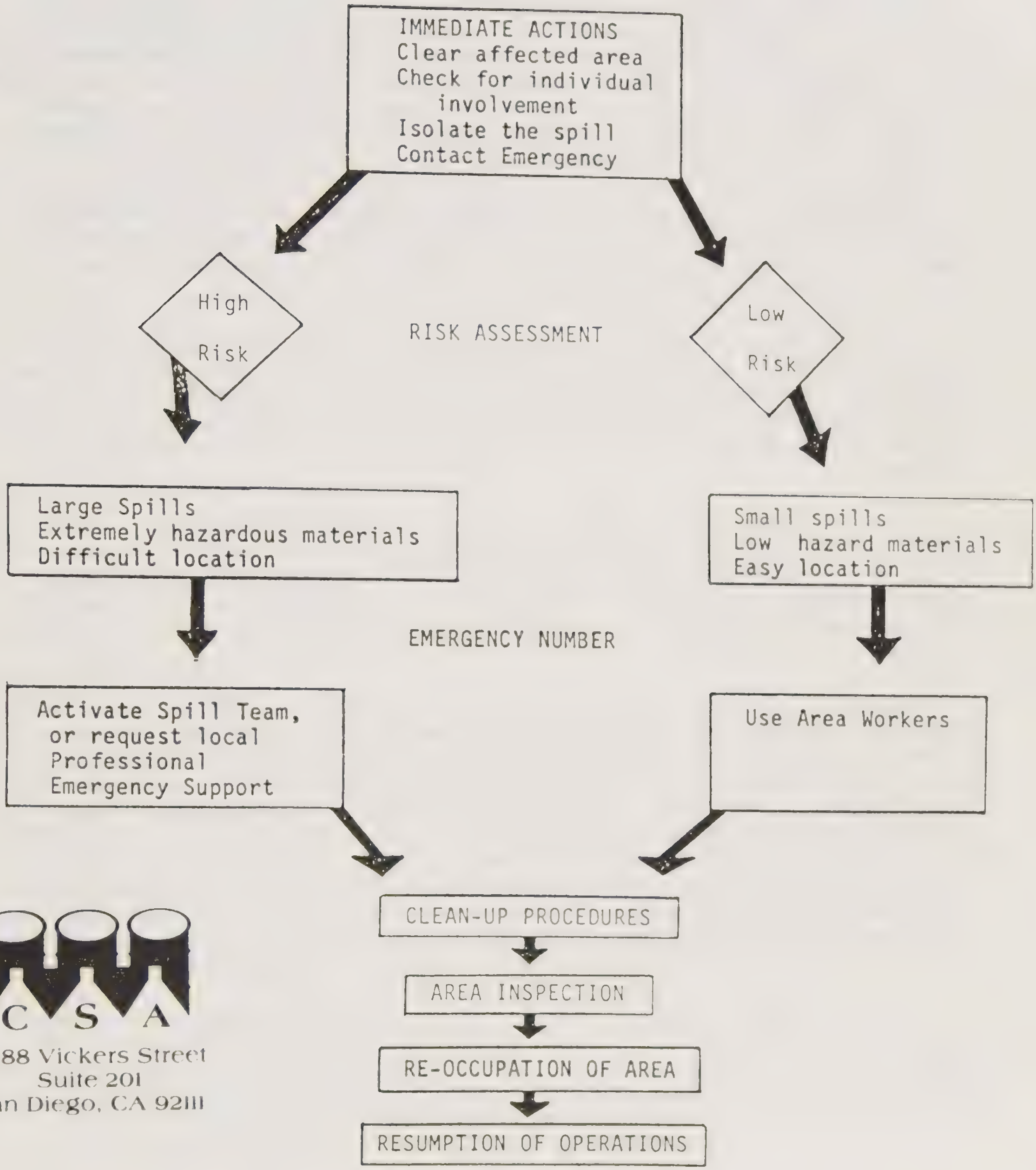
For spills involving oils, such as vacuum pump oil, a combination of SAFE STEP(tm) and polypropylene wipes will quickly and completely remove all oily residue. More serious spills, such as solvents, acids, and caustics, must be handled using very specific methods.

SOLVENT SPILLS

The options available for solvent spills are limited. A charcoal product, such as Baker Chemical's SOLUSORB(tm) is clearly the best choice, since it effectively controls vapors, thus reducing the fire hazard. However, it is very dusty. A superior choice is to evaluate the fire risk with a direct reading lower explosion limit meter (LEL) and then, if safe to use polypropylene wipes to absorb the free liquid while placing the solvent soaked wipes into a safety can. CSA uses a value of 25% of the LEL or higher as a cut-off. If the vapor concentration is above this 25% LEL value, the atmosphere must be modified by ventilation to reduce the concentration. Even under low concentration conditions, responders must be protected with high level fire protection, SCBA and fire retardant clothing, such as NOMEX(tm).

Solvent spills can be managed effectively. Trained personnel must understand the two very severe risks posed by the situation: flammability and toxicity. Proper procedures must be followed and effective sorbent materials must be used.

SPILL RESPONSE PROCEDURES



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ACIDS and CAUSTICS

Statistically, corrosive chemical spills comprise the majority of industrial chemical spills. According to preliminary data from the US EPA, the most common acids spilled are hydrochloric, sulfuric, and nitric. Sodium (or potassium) hydroxide and ammonium hydroxide are the most common caustics spilled. In the semi conductor cleanroom these materials plus various hydrofluoric acid related compounds are commonly spilled. In other situations, any of the above corrosives, plus many more may be released.

Traditional spill response procedures have involved using solid carbonate or bicarbonate materials to neutralize and absorb acid spills. Citric acid based materials have been used for caustics spills. These materials leave a difficult to manage solid residue and have the potential for producing large amounts of dust. For these reasons, plus many more related to the difficulty for decontaminating irregular surfaces, these solids have proved unsatisfactory.

The recent introduction of LIQUID ACID NEUTRALIZER (tm) and LIQUID CAUSTIC NEUTRALIZER(tm) has allowed the development of methods which greatly reduce the mess of such clean up efforts and lead to reduced disturbance of the clean environment.

The procedure is always followed on the "High Risk" path shown in Figure 1. The spill team will usually use SCBA, plus body, foot, and hand protection. Particular attention must be paid to the selection and use of gloves, since some of the non neutralized spilled materials will be absorbed on hand held polypropylene wipes. A minimum of double gloving is standard.

With at least three members of the team properly protected, a two person team penetrates the hazardous area. One person begins by controlling the source and diking the spill, if necessary, while the other person provides fire protection and support as needed. The third member of the team remains outside the hazardous area as safety and provides back-up support.

Specially treated non-dusting polypropylene wipes, booms, and dikes, which absorb water based solutions are used to mop up the spilled acid or caustic. These items are placed into plastic containers for later treatment. The contaminated area is now sprayed or wiped (with clean wetted polypropylene wipes) with LIQUID ACID (or CAUSTIC) NEUTRALIZER. The procedure of spraying and then absorbing the liquid is repeated until all of the acid (or caustic) residue is neutralized, as shown by the color change of the indicator in the LIQUID ACID NEUTRALIZER. The final step of the clean up is to use water to remove neutralizer and other residues. When these steps are performed correctly, the area is rapidly rendered non-hazardous and safe for maintenance and resumption of operations.

These procedures can be modified in many ways, as required by circumstances. In open, well ventilated areas, EPA Level C protection may be appropriate. For some spills, it may be more appropriate to neutralize the spilled chemical in place and then clean up the neutralized materials. In any event, circumstances must dictate the exact steps used.

Mention must be made of the health and safety characteristics of these products. Clearly, all chemical spills pose extra-ordinary risks to everyone involved. Care must be taken that the procedures and materials used do not increase the risks to unacceptable levels.

The liquid neutralizers are inherently low hazard chemicals. Material Safety Data Sheets for each material, which are readily available summarize the health and safety properties of the neutralizers.

The primary risk is the direct handling of the spilled chemical during the initial mop up. In so far as possible, this risk may be reduced by using plastic tongs to hold the wipes. Coupled to proper personal protective equipment, our observations indicate that this type of spill response is no more hazardous than traditional methods and much cleaner.

Chemical spills always require careful, planned response. The risks to responders and the inherent threat to human health and the environment can be controlled. During the past several years, the development of new methods and new materials for spill management have led to implementation of workable, cost-effective spill response programs.

GAS & VAPOR DETECTION

During Spill Containment

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ABSTRACT

The investigation, containment, and clean-up of Hazardous Material Spills presents the risk of dangerous gas or vapor exposure for an increasing number of industrial workers each year. Current EPA guidelines specify analytical equipment and techniques, but do not address the issue of worker health and safety during spill containment. A survey will be made of a broad range of currently available portable personal gas detection devices. Equipment such as combustible gas indicators, personal oxygen alarms, detection tube systems, chemically specific personal monitors, personal dosimeters (badges), and multi-function (TOXIC, COMBUSTIBLE, and OXYGEN) personal alarms will be discussed on the basis of cost, complexity and suitability. Recently proposed Confined Space Safety Standards at the State and Federal level will also be reviewed due to their relevance to the instrument selection process.

INTRODUCTION

Environmental Protection Agency regulations or guidelines frequently specify the methodology of gas or vapor analysis for such environmental concerns as air pollution, water pollution, stack emissions, and automobile exhaust. Traditionally, the Federal Occupational Safety and Health Administration (OSHA) has regulated the health and safety of workers at their place of employment - typically the fixed foundation factory or construction worksite. The Hazardous Spill clean-up scene such as a street, a river, a railroad track or waste disposal site, introduces an obvious jurisdictional "vacuum" with regard to worker exposure to toxic atmospheres:

1) Federal OSHA doesn't routinely visit the worksite (IT MAY LITERALLY BE A DISASTER SCENE!) Thus safety regulations are virtually non-existent.

2) The EPA specifies analytical measurements such as gas chromatography or photo/ionization for environmental analysis, but makes no provision for worker safety against explosive atmospheres, oxygen deficiency, or other hazardous substances in the breathing zone of the worker at a Spill site.

Into this vital environmental concern have rushed the worldwide gas detection instrument makers to (possibly) confuse the Spill Containment Community with such devices as: combustible gas alarms, detection tube systems, personal sampler pumps, personal dosimeter diffusion badges, personal toxic gas monitors, and even triple or quadruple function personal gas alarms for toxic, combustible, and oxygen deficient atmospheres. The purpose of this presentation is to review this rapidly expanding portable instrument field with regard to cost, complexity, specificity, sensitivity, and suitability for Hazardous Spill worksites.

(It should be noted at the outset that this discussion will not address the vast array of personal protective equipment (clothing, gloves, headgear, harnesses, etc.) now widely in use at spill sites. Nor will the discussion address the more complex issue of respiratory protection such as: cartridge respirators ("gas masks"); self contained breathing apparatus ("SCBA"); or supplied air respirators (SAR) which may be required at the Hazardous Spill worksite. It will only be emphasized that under OSHA, it is the employer's responsibility to insure a safe and respirable atmosphere for his employees. To ensure compliance with this requirement, the employer must test the atmosphere frequently, by whatever appropriate means are at this disposal, in order to specify what level of respiratory protection may be adequate. The common chemical cartridge respirator of "gas mask" now in wide usage in the Hazardous Spill industry is not approved for use in IDLH (Imminently Dangerous to Life and Health) atmospheres. Despite the wide usage, this form of respirating protection cannot protect against certain toxics (CO, H_2S, HCN,); may suffer "breakthrough" at higher levels of some toxics (ammonia); and may never be used in confined spaces or whenever there is a possibly of a lack of oxygen due to combustion, decomposition, or displacement by other gases. Only SCBA or SAR with 5 minute escape should be used when IDLH atmospheres are

suspected or identified. If the atmosphere cannot be measured on-site qualitatively for a suspected contaminate, presume the worst and presume IDLH atmospheres until measurements prove otherwise).

Since quantitative measurement of the atmospheres is critical to proper selection of appropriate respirator protection at Hazardous Spill sites, we will now review some of the personal gas and vapor detector offered in the market place.

<u>COMBUSTIBLE GAS INDICATOR</u> (Slides)

This type of personal portable gas detector has been in wide usage in mines, underground construction, and the below ground operations of public utilities for many years. Under such trade names as "Explosimeter", "Vapor Tester", or "Sniffer", these portable devices have been used to detect explosive levels of gases and vapor. The sensor principle uses catalytic oxidation (literally "burning" of the gas sample) on the surface of a catalyst coated bead operating at temperatures in excess of 1000°F. The burning phenomena leads to a further increase in the bead temperature, thus linerarly increasing the resistance of the heater wire to which the bead is bonded. The resistance increase is very small per unit change of gas concentration, so the devices are normally used for explosive gas mixtures which may contain 5,000 parts per million (ppm) to 50,000 ppm of the gas or vapor.

Sensitivity is poor for this class of device (concentrations below 200 ppm would be undiscernible) and specificity is non-existent (vitually all hydrogen and or hydrocarbon containing cases and vapors will react on the coated bead). Since many materials have established toxic limits as low as .1 to 10 ppm, this class of device has little to no value for atmospheric monitoring of hazardous materials other than suspected explosive materials in an open air environments. In confined spaces or otherwise oxygen depleted atmospheres, this class of instrument could totally fail to respond since the burning process on the catalytic bead requires oxygen levels usually above 15% to sustain combustion.

This class of instrument is still available in battery powered portable configuration for less than $500.00.

<u>PERSONAL OXYGEN MONITOR</u> (Slides)

Battery Powered Portable oxygen monitors generally use one of two types of wet chemistry cells to specifically detect oxygen gas: galvanic cells (Micro fuel cell) or polarographic cells. The galvanic cell generates a current at the two electrode terminals of the cell directly proportional to the partial pressure of oxygen in the ambient atmosphere around the cell. At the end of the useful life of the galvanic cell, its output current drops dramatically indicating the need for cell replacement (typically 9 to 12 months). No refurbishing of the sealed fuel cell is possible. A new galvanic cell stored in a nitrogen sealed pouch must be installed. Polargraphic cells work on small current change directly proportional to the oxygen concentration, about a base level of current through the cell. Since output current levels are lower than in the galvanic cells, the associated electronics is usually more costly and complex in this type of instrument. The polarographic cell, is however, reuseable when

periodically cleaned and recharged with a fresh electrolyte solution.

Personal portable oxygen monitors typically span ranges from 0-25% or 0-40% by volume oxygen. Since fresh air contains 20.9% by volume oxygen (balance nitrogen and other trace inert gases), the devices often are present to generate audio and visual alarms at 19.5%, the OSHA standard for an oxygen deficient atmosphere. Since the sensors in both types of oxygen monitors are based on wet chemistry, they are highly specific to oxygen gas and have virtually no cross sensitivity to reasonable levels of interferent gas species. The sensors require little to no power from battery packs, thus these units can be very small and lightweight (literally shirt pocket sized). Prices for such oxygen monitors may range from $400 to $600 for those using galvanic sensors, to over $800 for some with based on polargraphic sensor.

DETECTOR TUBE SYSTEMS (Slides)

The glass ampule detector tube sampling system shown in these slides is widely used by industrial hygienists, safety engineers, and environmental health experts for toxic gas analysis. These detector tube systems are relatively inexpensive (less than $250), simple to use, easily portable and relatively specific for over one hundred different gas and vapor species. Individual tubes cost about $2 to $3 each (sold in boxes of 5 to 10 to the box) and cannot be reused. Each measurement is made by breaking off both ends of the fresh tube, and drawing through the tube a precise volume of the atmosphere to be tested (often 100cc's of air). Each tube measurement is a one-time direct reading of that location for a specific contaminant. Chemical reaction times are typically 1 to 2 minutes and the user reads the gas concentration by the length of stain along the calibrated barrel for most tubes, or by a color comparison chart for certain other tube chemistries.

Detector tube chemistry permits such toxic gas measurements as:

(1) Formaldehyde as low as 1 ppm
(2) Hydrogen cyanide in the 1 to 100 ppm range
(3) Ammonia in the 1-20 ppm range.

Despite certain similarities in detector tube systems from the several makers of these devices around the world, NIOSH studies have shown that tubes from manufacture "A" should never be used with the pump from manufacture "B". That is, the maximum precision in a detector tube sampling program is achieved only by using the complete system from a given manufacturer and in accordance with the instructions provided by that manufacture.

Detection tube systems offer more "bang for the buck" - that is, a broader range of low level toxic gas and vapor detection, with a greater degree of chemical specificity, and at a lower cost per measurement than any other field portable gas analysis technique available today. Detector tube systems should, in my judgement, be a mandatory item in the safety equipment arsenal of every organization engaged in Hazardous Spill investigation, control or clean up.

PERSONAL SAMPLERS - CONTINUOUS PUMP & DIFFUSION BADGES (Slides)

Personal samplers for certain particles, dusts, gases and vapors are of two basic types: (1) battery powered sampling pumps; or (2) passive diffusion badges (dosimeters). The personal sampler pump is battery powered and operates as a sample draw pump worn on the belt of a worker throughout his workshift. The sampling hose is placed near the worker's breathing zone on a lapel or shirt pocket and draws a representative sample of air through either a paper disc or filter for dust or particle sampling, or over a charcoal tube for organic vapor monitoring. The disc must be weighed or optically analyzed for dust and particulate sampling, whereas the charcoal tube is sent to a laboratory for analysis by (usually) gas chromatography for certain gases and vapors.

It should be noted that both the types of monitors give management a very expedient manner in which to do industrial hygiene studies for TWA (Time Weighted Average) employee exposure to certain toxic materials over an 8 hour workshift or 40 hour workweek. They are of no safety value to the worker since they are inherently "silent" devices. Only readout by laboratory staff can subsequently identify and quantify employee exposive levels obtained by personal samplers of either type. These devices are truly "dosimeters", with no audio or visual alarm capability for worker safety in high gas or vapor environments. Because of this limitation such devices have little value to employee protection at Hazardous Spill sites. The sampling badges may cost only a few dollars, the personal sampling pumps may cost several hundred dollars - but both have the further cost and delay of laboratory analysis <u>after</u> the sampling period.

<u>CHEMICALLY SPECIFIC PERSONAL MONITORS</u> - For Toxic Materials (Slides)

In recent years a variety of chemically specific sensors for certain toxic gases and vapor have been developed. Instrumentation based on such sensors has been developed for such toxic materials as carbon monoxide (CO), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), chlorine (CL_2), and hydrogen cyamide (HCN). These sensors can be of two basic configurations: (1) wet chemical cells; (2) thin film solid state (wafer-like) sensors. The wet chemical cells rely on the choice of membranes, electrodes, and electrolytes to permit oxidation/reduction reactions which are highly specific to the gas species diffusing through the membrane and into the cell. The solid state film devices have etched film heater strips placed on the back of tiny ceramic "chips" only several millimeters in size. The electrode structure on the top of the chip is often coated with a proprietary chemical film layer which will result in conductivity changes between these top mounted electrodes which is proportional to the concentration of a toxic gas species diffusing through a sintered cup onto the film layer.

Chemical specificity for these sensors can be quite high, particularly for the wet chemistry type. Part per million (ppm) level detection or below is possible for some toxic gases. However, many such chemical sensors can be so selective for one gas species, that cross-sensitivity may be neglibly small for other possible toxic agents. Thus, these devices may

be almost analytical in nature and again not provide any measure of protection for a worker against flammable atmospheres, oxygen deficient environments, or presence of other materials which may be found in the area. Although sensor specificity is the key to successful environmental analysis, sensor specificity may lead to a disastrous worker SAFETY program!!

Chemically specific personal gas monitors may range from shirt pocket sized carbon monoxide monitors, to shoe box sized chlorine or hydrogen sulfide detectors. Prices may range from a few hundred dollars to several thousand dollars. It is a fast-moving field and potential purchaser should ask many questions of instrument makers regarding sensor life (and replacement cost), frequency of calibration, temperature limits, and cross sensitivity.

MULTI-FUNCTION PERSONAL GAS ALARMS (Slides)

In this class of portable gas detector, instrument manufacturers use a multiplicity of gas sensors with a single power pack and complete the instrument with analog or digital displays, audio and visual alarms, and (possibly) some remote sampling probe. Typically such instruments have: (1) a wet chemical sensor to respond specifically to oxygen; (2) a solid state or wet chemical sensor for certain toxic gases and vapors (CO, H_2S etc.); and (3) a catalytic bead or metallic oxide semiconductor (MOS) sensor for broad range combustibles response. Thus, a single multifunction portable gas detector offers worker protection against three major hazards - oxygen deficiency (or enrichment), toxic gas and vapor, and combustibles. The toxic sensor in some models may be of the chemical type and thus highly specific for only one gas species. Other manufacturers may use multiple toxic sensors or the broader range of the MOS sensor in order to obtain response to numerous toxic gases and vapors. Instrument size for these units may range from hand-held ("walkie-talkie" size) to shoulder strapped units weighting 3 to 4 pounds. Prices may range from \$800 to over \$2000 for such multifunction instruments.

The instrument development activities in this field are perhaps the most active of all the gas detection concepts surveyed in this presentation. This is not due to the market demand represented by the Hazardous Spill Industry, but rather by the development of various State and Federal regulations regarding so-called "CONFINED SPACE ENTRY" operations. A confined space in its most generic meaning is a space: (1) not intended for continuous employee occupancy; (2) having limited or unavailable natural ventilation; or (3) containing suspected dangerous air contaminants including oxygen deficiency, toxic materials, and combustible gases and vapors.

In addition to the rigorous safety procedures and the extensive worker training procedures required for confined space work operations, the various State and Federal regulations require atmospheric monitoring for all three forms of air contaminants prior to entry and sometimes on a continuous basis. It should be noted that many aspects of Hazardous Spill investigation and containment could be interpreted to fall under such confined space safety standards. In such cases, this industry would be well-advised to give serious consideration to this class of multifunction portable instrument for the maximum level of worker health and safety.

ODOR PERCEPTION AS AN AID TO CHEMICAL SAFETY IN THE WORKPLACE

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Threshold Limit Values

Over the years, industrial hygienists have collected data on the harmful effects of chemical vapors in the workplace. By measuring the average exposure concentration of a given chemical that was considered responsible for damage, a "threshold limit value" or TLV was established as a guideline for preserving worker health and safety. Usually these are 8-hr. time-weighted average concentrations. Most of the TLV values currently recognized in U.S.A. were originally recommended by the American Conference of Governmental Industrial Hygienists, ACGIH (1). They have now, with occasional adjustment, been given the force of law by the Federal OSHA and Cal OSHA (permissible exposure limits, PEL).

Nevertheless, it is always a problem to ascertain whether a given workplace environment complies with the regulations. The 8-hr. average provision requires prolonged and/or intermittent air sampling, followed by instrumental or detector-tube analysis. Indicator badges or diffusion tubes, as well as absorber badges with subsequent analysis, can also provide the necessary information, but after long delays. Some instruments can operate on grab-samples of air, or even monitor continuously in real-time, but tend to be cumbersome and expensive. Firms that do not employ their own industrial hygienist, and are hesitant to call in a consultant or inspector, may be at a loss to know whether there is any chemical hazard in their operations.

Often overlooked as a potential "warning system" is our sense of smell. With very few exceptions, the nose can detect any of the volatile substances on the PEL lists. Therefore, if the worker can detect the odor of a chemical in his workplace, he must be breathing at least some significant quantity of the vapor. The question is, whether that amount exceeds the harmful limit. Considering that nearly everybody has a functional sense of smell, that monitors precisely the air we breathe, responds instantly, and costs nothing, there seems to be considerable incentive to explore its potential for contributing to worker safety.

Odor Thresholds

This was the starting-point for a recent Review article by Amoore and Hautala (2), in which this concept is thoroughly developed. The threshold of odor detection is the lowest concentration of a substance in air that can be detected by just half of the people tested. A search of the world's literature yielded published odor thresholds for 214 of the substances on the ACGIH TLV list of 1982. In fact, for many substances, multiple reports were available, which were averaged to provide a single best value for each compound.

To place the results in perspective, and for maximum utility to industrial hygienists and pollution control engineers, the data on all 214 compounds were assembled in a Table with 14 columns of numerical values. The application of odor threshold to worker safety will be illustrated here for two substances at opposite ends of the "odor safety" scale, amyl acetate and carbon tetrachloride:

Property	n-Amyl acetate	Carbon tetrachloride
Threshold limit value, ppm	100	5
Odor threshold, ppm	0.054	96
Odor safety factor	1800	0.052
Odor safety class	A	E

Amyl acetate, or "banana oil" is considered safe enough to use for testing the fit of a respirator mask to the face. With its TLV of 100 ppm, and odor threshold of 0.054 ppm, it can be detected by an average person at 100/0.054 or about 1800 times lower concentration than its permissible exposure limit. For carbon tetrachloride, in contrast, the odor threshold is much higher than the TLV, and the odor safety factor is virtually non-existent, 5/96 or 0.052. These observations indicate that some chemicals, like amyl acetate, can be smelled easily at much lower concentrations than are believed to be harmful, whereas others, such as carbon tetrachloride, have so little odor that if they can be smelled at all, they are already far above the permissible limit for safety.

Another factor to be considered is that of attentiveness. The conventional odor threshold refers to what people can achieve, under laboratory conditions, when they are making a conscious, directed effort to detect an odor. When people are inattentive, and especially when their attention is distracted by a demanding task, they may not even notice a distinct odor that is strong enough to be obvious when they are asked to give it their full attention. This factor is very important in odorization practice for natural gas and bottled gas, and was researched by Whisman et al. (3). From their results one can deduce that when people's attention is distracted, they require on average 26 times higher odorant concentration than would be their detection threshold under conventional test conditions.

Odor Safety Class

We have taken into consideration the TLV, odor threshold, and the variable of attentiveness, to evaluate the potential warning properties of each compound for which olfactory data are available (2). The odor safety factor is a numerical ratio, in which the higher the value, the greater the degree of odorous warning, of its presence in the air at a harmful concentration, is provided by the chemical. For the interpretation of this value, we have set up a provisional scale of odor safety classification, with a letter code assigned to each of the 214 compounds, on a scale from A for the greatest warning power, to E for the weakest.

Compounds in class A, such as certain esters, have an odor safety factor over 550, indicating that more than 90% of people would perceive the odor of the TLV concentration in the air, even when their attention was distracted by a demanding task. Substances in class C, with odor safety factor between 1 and 26, would be noticed by less than 50% of people engrossed in some task. At the other end of the scale, class E compounds such as certain chlorinated hydrocarbons with odor safety factor below 0.18, could be detected at their TLV concentration by less than 10% of people even making their best effort to perceive the odor. The class B and D substances take their intermediate positions in the scale.

The main Table in the previously cited paper (2) provides additional data relating to the odor detectability and safety factors for each of the 214 compounds. The safe dilution factor indicates how many volumes of clean air would have to be mixed with one volume of air saturated with the vapor of the compound at 25°C (for example, in a spill) to reach the TLV dilution. Equivalent data on TLV and odor threshold are provided for solutions of the compound in water at 25°C. The volatility, water solubility, water/air distribution ratio, and acid dissociation constant (if applicable) are also recorded for 25°C.

Education of Workers about Odor Safety

We believe that these principles can be applied to assist with preserving a healthful workplace environment. If workers could be informed of the odor safety classifications of any substances with which they work, it would provide some helpful guidelines. For example, workers with class A substances could be reassured that the mere presence of a mild odor does not necessarily mean that harmful concentrations are present; in all likelihood, the TLV is far from being reached. Conversely, they should be advised that if they ever detect the odor of a class E compound, it is almost certainly over its recommended TLV, and precautions should be taken to avoid any further inhalation (use of vent fan, respirator, etc.).

Unfortunately, in practice, the application of this concept is not entirely straightforward. People are not all exactly alike in their sensitivity to odors. In fact, even among healthy people there is a wide range of sensitivities (2). In a group of 100 people, there is a normal distribution of sensitivities, with approximately 16% being

more than 4 times as sensitive as the average, and another 16% being less than $\frac{1}{4}$ as sensitive as the average. Besides this variation, other factors such as a head cold or nasal allergy can reduce sensitivity another four-fold.

The effects of these natural variations could be largely compensated, and olfactory assessment of the environment made very much more precise, by providing odor standards for comparison. It would be very helpful if we could demonstrate to each worker the actual experience of smelling the chemical at its TLV concentration in the air. Then, if the smell at the workplace was weaker than the standard, there would be no need to be concerned; but if the surrounding odor was stronger than the standard, then process alterations or respiratory protection is necessary to restore a healthful work environment.

There are several ways that such odor demonstrations could be provided. We suggested (2) the preparation of an aqueous solution of the substance (in a stoppered flask) that could be sniffed to experience the PEL concentration. Our Firm (Olfacto-Labs) has developed odor threshold test kits with shampoo-type squeeze-bottles containing mineral oil solutions of odorous substances (4), and we believe that this method could be adapted to provide ready-for-use odor demonstration kits for PEL concentrations of various compounds. We also have under development a compact portable vapor generator, that is capable of delivering an air-stream containing adjustable ppm concentrations of the chemical under test. This type of instrument, generally known as an "olfactometer", has the advantage of providing a more natural experience of the odor intensity sensation.

Whatever method is selected for exhibiting the standardized odor intensity, the important point to remember is that it should be coordinated with an educational program for the workers, under the guidelines of worker safety and right-to-know regulations. In that way the maximum benefit to the chemical worker can be realized.

Odorization for Safety

There are a number of potentially dangerous substances in use in commerce and industry that have little or no inherent warning properties, for example, natural gas (methane) and bottled gas (propane). In recognition of the explosion hazard for the general public, regulations require that these gases be odorized. The industry adds sufficient odorant, usually mercaptans or sulfides, to provide an odor safety factor of about 500-fold, if the gas should leak and reach its lower explosive limit in the air. The same concept has recently been extended to cryogenic oxygen in several European shipyards, where dimethyl sulfide is added as a leak indicator, that gives a relatively low odor safety factor of about 18 if the oxygen enrichment reaches 2%. The success of this program, despite a seemingly low odor safety factor, is probably due to systematic worker education, so that the shipyard workers are able to respond to odor detection, without the necessity for a 26-fold

increased odorant concentration that would be required to overcome the factor of distracted attention among the general public.

Another class of dangerous gases and vapors are the simple asphyxiants, particularly the denser-than-air argon and Freons. We are aware of two recent suits in which there was suffocation of workers by low-lying pockets of escaping gas or fumes. In each case the attorney for the plaintiffs argued that the accidental deaths could likely have been prevented, had the inert gas been odorized as a warning. Both cases were settled, so no legal precedent has been established. Nevertheless, an important principle has been brought out, that if odorization technically could be applied to increase the safety of using a particular product, then perhaps it should be odorized. The same principle applies to other hazardous chemicals, and to many pesticides, which may have insufficient natural odor to provide an adequate safety factor.

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AN INTEGRATED APPROACH TO AIR MONITORING AT HAZARDOUS WASTE SITES

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INTRODUCTION

Hazardous waste site investigations and remedial activities often involve airborne exposures to multiple chemical species. Successful evaluation of these air contaminants is predicted upon first defining the full range of exposures which may be present and then determining the monitoring methods required for adequate characterization. This task is often complicated by lack of precise information regarding existing site conditions and the dynamic nature of exposure generation resulting from site activities.

Air Monitoring Strategy

The objectives of a hazardous waste site air monitoring program and the corresponding sampling strategies are presented in Table 1. Evaluation of protection levels is achieved primarily through the use of direct-reading instruments. Sampling techniques based on NIOSH validated methods often provide better qualitative and quantitative results than are available through the use of the real-time instruments. Integrated sampling techniques permit a time-weighted average evaluation of employee exposure levels, as required by OSHA standards. Samples can also be collected for contingency purposes. These samples are usually analyzed only when an unexpected release or exposure occurs.

Exposure Identification

Defining the types of chemicals which may be encountered during the waste site work provides the framework for evaluating monitoring needs. This task is accomplished through a comprehensive analysis of the site characteristics. Important sources of information include records of waste management practices, interviews with knowledgeable parties, and data from previous environmental studies.

The derived information on contaminant types and quantities is then analyzed in terms of anticipated exposure levels. The physical and chemical characteristics of the contaminant and its environment provide the basis for this analysis. Of particular concern are those processes associated with the proposed site work which will increase the probability of exposure.

Volatilization of organics from mechanically disturbed or exposed soil and water media is an obvious source of airborne exposure during waste site work. Estimating the extent of these exposures will assist in choosing the proper monitoring equipment and/or the required sample volumes.

The rate of gas and vapor volatilization from a water media is primarily a function of solute vapor pressure, temperature, solubility and air current velocities. Evaporation rates from soils are additionally affected by the octanol partition coefficient, soil porosity, tortuosity and organic carbon content (Jury, 1983).

The saturated vapor pressure of a volatile contaminant can be used to estimate worst-case exposures near the soil/air or water/air interface. Studies have shown that extremely low concentrations of semi-volatile contaminants in soil are able to produce a saturated vapor density at the soil/air interface (Farmer, 1972).

Exposure levels from contaminated groundwater and soils which contain an appreciable moisture content can also be estimated using Raoult's Law and Henry's Law. Raoult's Law is most applicable to compounds with low aqueous solubility:

$$Yi\ P_{ATM} = Xi\ P_{SAT}$$

P_{SAT} = Vapor pressure of solute at specified temperature
P_{ATM} = Atmospheric pressure
Xi = Mole fractions of solute in solution
Yi = Mole fractions of solute in air

Henry's Law considers the solubility of the contaminant in describing the partitioning relationship between air and water:

$$Cv = H\ Cl$$

where Cv = Concentration of solute in air
Cl = Concentration of solute in liquid
Hc = Partitioning coefficient (Henry's Constant)

and $$Hc = \frac{C\ air}{C\ water} = \frac{16.04\ P^{\circ}M}{T.S}$$

where P = Vapor pressure of solute at specified temperature
M = Molecular weight of solute
T = Specified temperature ($^{\circ}K$)
S = Solubility (mg/l)

The above exposure estimating methods generally provide worst-case predictions of airborne concentrations. Dispersion and dilution is not considered. In addition, vapor releases in soils may be retarded by adsorbtion/absorbtion and physical barriers related to the tortuosity.

More sophisticated modeling approaches are sometimes warranted. Model inputs include site-specific meteorology, micrometeorology, hydrology, water and soil chemistry, topography, and location of man-made structures (Thibodeaux, 1982). Computer programs are available which can estimate downwind concentrations based on these variables. Chambers have been developed which can measure the mass flux of organics from soils at various wind velocities.

Non-volatile contaminants contained in soils can become airborne through wind and mechanical disturbances. However, the magnitude of such exposures can not be easily estimated. Important factors affecting the potential airborne concentration of the contaminant include the concentration, extent of binding, soil moisture content, and of course the type of disturbance (e.g., wind, digging, drilling, etc.).

Defining Monitoring Strategies

Under ideal circumstances all of the airborne contaminants present at the waste site would be monitored using a combination of real-time instruments and air sampling methods, including GC/MS analysis. Unfortunately, it is often only feasible to monitor for those contaminants which are believed to have the greatest potential for adverse exposure.

The contaminants' toxicity, estimated extent of exposure and proposed control measures are the primary factors affecting the extent of air monitoring required. For example, the monitoring methods may concentrate on those compounds which are not efficiently controlled by the designated level of respiratory protection. Similarly, the monitoring strategy may concentrate only on the most toxic compounds when it is believed that the other, less harmful contaminants are adequately protected against.

Case Study

A soil boring and groundwater sampling program was to be conducted in disposal areas containing a variety of hazardous wastes associated with an organic chemicals production facility. Thirty soil borings would

be drilled to depths ranging from 15 to 35 feet and sampled at 5-foot intervals. Groundwater samples would be collected from existing on-site extraction and monitoring wells.

As discussed, selection of the appropriate air monitoring methods is predicted upon recognizing the specific types of chemical exposure potentials. The U.S. EPA, state and local agencies had commissioned several studies at this site which provided a comprehensive overview of waste disposal practices, hydrology, geology and groundwater quality. Information pertinent to airborne exposures and monitoring strategies is summarized below.

The plant is located in an arid climate, however, a shallow perched aquifer exists beneath the disposal sites. Large quantities of liquid and solid wastes associated with the production of organophosphates, chlorobenzenes, and lindane were disposed on-site during a 30 year period. Disposal methods consisted of leach fields, evaporation ponds, pits and surface piles. Dioxins had been detected in surface soils and were believed to be associated with the chlorobenzene stillbottoms.

In 1978, 30,000 gallons of benzene leaked from an underground storage tank. A series of monitoring and extraction wells was installed as part of the remedial action. Sampling results indicate that the plume is traveling northward, through the disposal areas.

Personal protective equipment consisted of the following devices: full-face, powered air-purifying respirators with pesticide/organic vapor cartridges, Saranex® suits with attached hoods and booties, Viton® gloves, and neoprene boots. Due to the potential for offgassing from buried drums and the close proximity of a chlorine plant, five-minute escape masks were positioned at the upwind staging area of each boring site.

Based on the available information on the site characteristics, each of the identified chemicals or chemical groups was analyzed in terms of its airborne exposure potential. Air monitoring strategies were then developed based upon comparison of estimated exposures to exposure guidelines and the degree of protection afforded by personal protective equipment.

Table 2 summarizes the air monitoring strategies for this site. The remainder of this paper describes how the decision logic framework for developing the air surveillance protocols.

1. Benzene: Previous groundwater investigations determined that benzene was migrating throughout the disposal areas. Exposures to benzene vapor were anticipated when sampling groundwater and soils from the vadose zone.

Monitoring wells within the disposal areas contained between 16 and 2,300 ppm benzene. Henry's Law was used to estimate the airborne concentration of benzene from groundwater and soils extracted from the vadose zone. Based on an anticipated ambient temperature of 77^{O}F, Henry's Law constant for benzene equals 0.17. Thus, an air/water (or air/soil) interfacial concentration of 391 ppm is obtained from a substrate benzene content of 2,300 ppm.

The HNu Systems photoionizer instrument was chosen to provide real-time data on benzene exposures. The 10.2 eV probe has an excellent response to benzene vapor and the instrument requires only a few seconds to reach a 100% reading.

The protection factor afforded by the chosen respiratory protection provided a significant margin of safety (adequate to 2,500 ppm benzene, based on a protection factor of 250 and a TLV of 10 ppm). However, due to the relatively high toxicity of this compound and its widespread occurance throughout the site, integrated air sampling based on the appropriate NIOSH method (charcoal tubes) would be conducted, primarily for documentation purposes.

2. Chlorobenzenes: The chlorobenzene disposal area contained stillbottoms from production vessels and equipment. The vapor pressure of these compounds is much lower than benzene, however, vaporization of the lower chlorinated species could be expected from heavily contaminated soils. The photoionizer detector is also sensitive to chlorobenzenes and was chosen for real-time monitoring. (The action level, based on benzene and the potential for coevaporation of pesticides, would be adequately protective against chlorobenzenes, which have higher TLV's.) The charcoal tube samples would be analyzed for chlorobenzenes in addition to benzene, if the average breathing zone exposures exceed 10 ppm, based on photoionization detector readings.

3. Miscellaneous Volatile Organics: Benzene and chlorobenzene were the only volatile organics anticipated to cause measureable exposure levels. However, the photoionizer detector is responsive to a wide variety of other volatile compounds. A contingency was therefore developed for performing GC/MS analysis on the charcoal tube samples when photoionization detector readings exceeded 10 ppm in the breathing zone for greater than 30 minutes.

4. Dioxin: Trace levels (<1 ppm) of dioxin were believed to be associated with the chlorobenzene disposal areas. Since dioxin has a minimal vapor pressure and is known to adhere tightly to soil particles exposures would be expected to occur only in the form of aerosols. Ecology and Environment, Inc. has had extensive experience in investigating dioxin contamination at over 50 waste sites while assisting the Environmental Protection Agencies' National Dioxin Study. This background has resulted in a standard operating procedure for performing

ambient monitoring at dioxin sites. The ability to implement a qualitative and quantitative sampling method was limited by the required sample volume (greater than 160 cubic meters), laboratory turnaround time (1 week minimum) and analytical costs ($1,000 per sample).

A feasible alternative to a specific sampling method was derived through the use of an indirect exposure measurement technique. The portable, direct-reading aerosol monitors could be used to measure the concentration of total particulates present in the breathing zone. Exposures are thereby assessed by estimating the maximum probable concentration of dioxin contained in the total particulate.

5. Organophosphates: These compounds were buried in leach fields and open pits. The extremely low vapor pressure of these compounds, combined with their occurance in subsurface soils of high moisture content, limited the potential for airborne exposures. Further, these compounds are expected to readily break-down in soil and water. Therefore, no specific air monitoring was conducted for the organophosphorous compounds (strict personnel decontamination procedures were however implemented to reduce the potential for skin absorption).

Organophosphates contain reduced sulfur which could be potentially released as hydrogen sulfide (Myers, 1985). H_2S exposures would therefore be monitored with direct-reading colorimetric tubes while drilling in the organophosphate disposal areas.

5. Lindane: While lindane has an extremely low vapor pressure, a particulate exposure was anticipated during drilling. 200,000 cubic yards of lindane waste was located in an above-ground pile. Airborne exposures to lindane were expected to be much higher than exposures to organophosphates since the former wastes were more concentrated, located well above the water table, and are not subject to rapid degradation. There also existed less protection against the strong desert winds when working on the elevated mound of lindane.

The aerosol monitor would also be used to monitor lindane exposures. Readings would be equated directly to estimate the lindane concentrations; these readings would then be compared with the applicable exposure guidelines. In addition, integrated air sampling would be conducted based on NIOSH method S290 for exposure documentation purposes.

SUMMARY AND CONCLUSIONS

Development of a comprehensive air monitoring strategy for waste site work is required to satisfy the various objectives related to health and safety surveillance. The case study illustrates the need to integrate available information on exposures, controls and appropriate monitoring methods in developing a successful program. Available data and information on the site characteristics and proposed activity are

analyzed to develop risk estimates. Air monitoring strategies are then developed based on the types and severity of identified exposures. The resulting program usually incorporates a variety of monitoring methods; each of which may have singular or multiple applications in monitoring the identified contaminants.

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Table 1

AIR MONITORING STRATEGY CONSIDERATIONS

OBJECTIVES	SUGGESTED APPROACHES	INSTRUMENT/ EQUIPMENT CRITERIA
LEVELS OF PROTECTION - upgrade or downgrade respiratory protection or protective clothing based on preset action levels.	a. time-integrated personal sampling b. real-time direct reading class or species-specific area monitoring with audible alarm or observer; species characterization backup instrumentation.	o Personal Sampling - sensitive to low concentrations at designated sampling rate and volume - long service life (+10 hours) o Area Monitoring - sensitive at low concentrations in relation to established action level - short response time (<10 seconds) - species characterization capability preferred
ACTION LEVELS - detection of ambient concentrations for the purpose of mitigation of on-site emissions or off-site evacuation.	real-time continuous area monitoring with audible alarm at preset action levels or with observer; species characterization backup instrumentation	- sensitive in the sub-TLV range - class or species-specific capability - short response time (10 seconds) - long service life 10+ hours

Table 1 (Cont.)

OBJECTIVES	SUGGESTED APPROACHES	INSTRUMENT/ EQUIPMENT CRITERIA
		- direct reading real-time - sensor sensitive to most toxic indicator contaminant in multi-contaminant environments
CONTINGENCY EXPOSURE VERIFICATION - qualitative and quantitative contaminant determination in the event of accidental chemical exposure known or unknown volatile agents.	near real-time quantitative species-specific determination of ambient air representative of exposure; single step on-site analysis or dual step on-site sample collection with off-site analysis	o species-specific capability (preferably within 10%-20% accuracy) at TLV levels - sensitive at order of magnitude less than TLV - short warm-up period - rapid analysis - calibration stability - field portable instrument or sample
AMBIENT AIR CONCENTRATION DOCUMENTATION - verification of contaminants in ambient air over life of remedial action for legal and public health documentation purposes.	a. real-time instruments with strip chart recorders b. time-integrated active/passive sampling with sorbent/filtration media;	o Direct Reading Instruments with Recorders - class-specific capability - sensitivity contingent on contaminant (ppt to ppm)

Table 1 (Cont.)

OBJECTIVES	SUGGESTED APPROACHES	INSTRUMENT/ EQUIPMENT CRITERIA
	peak and average concentrations determined based on NIOSH methods	- strip chart or magnetic tape recorders - sensor sensitive to indicator contaminant o Time-Integrated Sampling - capable of handling long duration sampling - multi-media sampling train - adjustable flow rates - capable of high volumes

Table 2

CASE STUDY - AIR MONITORING METHODS

COMPOUND	MONITORING STRATEGY
Benzene	Photoionization Instrument (Real-time evaluation of protection and action level monitoring)
	Integrated Air Sampling (Documentation)
Chlorobenzene	Photoionization Instrument
	Integrated Air Sampling (Documentation)
Miscellanceous Volatile Organics	Photoionization Instrument
	Integrated Air Sampling (Speciation of contaminants)
Dioxin	Aerosol Monitor (Real-time evaluation)
Organophosphates	Colorimetric Tubes (H_2S offgassing)
Lindane	Aerosol Monitor (Real-time evaluation)
	Integrated Air Sampling (Documentation)

INDOOR AIR SAMPLING FOR VOLATILE ORGANIC COMPOUNDS ASSOCIATED WITH ENVIRONMENTAL CONTAMINATION

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INTRODUCTION

Volatile components associated with environmental contamination from a variety of sources can threaten public health and safety. These sources include spills and loss of manufactured chemicals and petroleum products as well as storage, treatment, and disposal facilities (landfarms, surface impoundments, and landfills) for hazardous and non-hazardous materials. A related problem involves the discovery of contaminated soil (oil fields, discharge areas, and landfills) under or near new residential developments.

Subsurface environmental contamination can impact workers and/or residents inhabiting structures near or above contaminated areas. Volatile compounds (and to a lesser degree aerosols), can migrate and infiltrate into structures through ventilation service, utility connections, conduits, cracks in the foundation, and structural defects. A systematic approach has been developed to identify and monitor air contaminants in structures related to subsurface contamination. Results can be used for exposure assessment as input to the design of exposure mitigation measures and to help define the nature and extent of the environmental contamination. This paper presents a general sampling and analytical scheme to conduct this type of monitoring. Structure surveys associated with volatilization and migration of vapors from releases of petroleum hydrocarbons will be given as specific examples.

A flow chart is used to guide structure sampling. The flow chart is designed to provide characterization of indoor air quality at breathing zone height and identification of point sources of air contamination. All data are collected and documented such that subsequent sampling and/or routine monitoring generate a consistent data base. Data evaluation and interpretation techniques, including the use of quality control and control structure data, are discussed.

TYPES OF STRUCTURE SURVEYS

In general, two types of surveys may be defined, the investigative survey and the routine monitoring survey. The techniques employed and the type of results that are obtained depend on the structure survey selected. The objectives of the monitoring program dictate which type of survey is selected. Figure 1 shows the relationship between

investigative and routine monitoring surveys, and a description of each is given below.

Investigative Surveys

These surveys are designed to provide emergency response information or discovery information. Screening techniques (Level A) are employed to identify structures where the presence of environmental contamination threatens occupant health or safety. Results of the investigative survey are the yes/no type (presence or absence) based on real-time protection criteria. Follow-up activities may include remedial (mitigative) action, evacuation, or continued routine monitoring.

Routine Monitoring Surveys

Routine monitoring is designed to provide surveillance of ongoing potential hazards and to assess the character and variability of hazard severity over time and with respect to these factors. A multi-level analytical approach is cost-effective and provides a variety of indoor air quality data. Screening techniques (Level A) are supplemented by integrated sampling (Level B) and to a lesser extent, detailed analysis (Level C). Results of the routine monitoring survey are indoor air contaminant identification and quantification over time. These data can be used to describe potential exposures, guide remedial investigation activities, and/or may be released to concerned parties to put the problem in perspective. The data base generated by this type of survey can be complete and unbiased, and the data can be readily used to observe trends in air contaminant levels according to type of structure, location, or other variables.

The routine monitoring survey can be augmented by increased-frequency monitoring in the event that indoor contaminant levels exceed established action criteria. In this case, it may be desirable to increase the proportion of Level C analyses in order to determine the nature and the source of elevated levels.

Routine monitoring surveys are usually continued for a predetermined period after which decreased-frequency monitoring may serve as a follow-up activity.

Selection of Sampling and Analytical Techniques

Design of an effective sampling approach generally employs one or more of the following techniques for measuring key parameters: 1) real-time monitoring using portable instruments; 2) discreet, real-time measurements and inspection; 3) integrated sample collection and analysis; and 4) grab sample collection and analysis. A combination of these is usually required for a complete cost-effective monitoring program. Routine monitoring surveys are designed for sampling in a consistent number and type of locations. Sample collection or measurement techniques must be uniform throughout the program. For instance, repeat sampling should be scheduled for the same time of day to reduce variability associated

with structure use. Consistency in these areas warrants special attention during design stages so that uncontrolled variability does not limit the use of the data.

A multi-level sampling and analytical approach is well suited to most indoor air sampling. Table 1 lists possible multi-level sampling and analytical techniques along with general advantages and disadvantages that must be considered in technical approach design. Real-time analysis using portable instruments can provide screening data that determine the need for more detailed or higher level analysis. Survey design may also include mid-level analysis techniques as a cost-effective means of confirming results or distinguishing target from non-target parameters. Detailed or specialty analyses generally provide the greatest accuracy and precision, particularly at low levels, and may require the use of sophisticated sample collection techniques. The cost and turnaround times associated with these analyses are also greater, and it is desirable to minimize the number of samples analyzed by level C techniques.

Table 1 includes the sampling and analytical techniques (indicated with stars) used for the structure surveys described at the beginning of this section. Level A analysis consists of real-time monitoring for THC using a portable organic vapor analyzer. Level B analysis consists of eight-hour charcoal tube collection and analysis by gas chromatography with flame ionization detection, providing time-weighted average concentrations of C_4 through C_{12} hydrocarbons. Detailed hydrocarbon speciation is provided by Level C analysis of evacuated canister samples (either grab or integrated sampling) using a gas chromatography technique and multiple detectors (flame ionization, photoionization, and electrolytic conductivity). The proportion of each level of analysis required for characterization is dictated by the results of the previous survey activity according to the flow chart in Figure 2.

SURVEY DESIGN

The following discussion emphasizes the design of routine monitoring surveys. These general techniques can be modified for use in investigative survey design according to specific project requirements.

Design of the structure survey should include periodic monitoring for key parameters at breathing zone height and at likely point sources of contaminant infiltration. A flow chart is used to guide sampling based on survey results at each stage. An example of a flow chart is given in Figure 2. This diagram shows the strategy used to monitor for indoor air contamination resulting from a release of liquid hydrocarbons. Results obtained by measuring for total hydrocarbon (THC) concentration using a portable real-time organic vapor analyzer (OVA) indicate the survey schedule to be employed.

A detailed preliminary survey of each structure is recommended to initiate contact with the owner or resident and to document and "code" the layout of rooms and the orientation of the structure. The structure may be assigned grid points if mapping of impact is an objective.

TABLE 1.

MULTI-LEVEL SAMPLING AND ANALYTICAL APPROACH

Level	Possible Sample Collection Techniques	Advantages	Disadvantages
SAMPLING:			
A	Real-time portable analyzers* Visual observations Olfactory observations	Portability, durabiltiy, low maintenance, minor training requirements, real-time results, low cost.	Relatively low accuracy and precision, non-specific detection
B	Sorbent* (routine, commercial tube) Head space (solid, liquid)	Standard techniques, some speciation data, time-weighted data, moderate cost	Limited speciation, moderate level of accuracy and precision
C	Sorbent (non-routine) Syringe (stainless steel, glass) Bottle (glass vessel) Bag (tedlar, teflon) Bomb* (stainless steel)	Detailed speciation and quantitation, can identify source of vapor, good accuracy and precision	Relatively high cost, requires trained sampler, slower turnaround time

Level	Possible Analytical Techniques	Advantages	Disadvantages
ANALYTICAL:			
A	Real-time or screening analysis; flame ionization detection*; photoionization	Short turnaround time, relatively low cost	Relatively low precision and accuracy, non-specific
B	On-site analysis for: total quantities*; select species (flame ionization, photoionization)	Relatively short turnaround times, moderate cost, moderate detection capability	Potential training requirements, equipment purchase and maintenance
C	Off-site analysis for: total quantities; select species; complete, detailed species* (multiple detectors including mass spectroscopy)	Maximum accuracy and precision, quantitation of individual tracer, species, low detection limits	Relatively high cost, shipping requirements, long turnaround times

* These techniques were employed for the example residential structure surveys.

The minimum, "routine" sampling schedule includes sampling in a representative, consistent set of rooms on a regular basis. If action criteria limits are exceeded, increased monitoring may include more frequent surveys or sampling in more rooms. An increased proportion of detailed analyses (Level C) may also be required.

Elements in the flow chart, such as action criteria limits and schedules, are selected by applying the design techniques described below. The example in Figure 2 will be used to illustrate these techniques.

Selection of Monitoring Parameters

In some cases, the contamination source is complex, and structure survey design must include selecting a limited number of key parameters for monitoring. This selection should involve consideration of the following: 1) program objectives; 2) health and safety concerns; 3) prior knowledge of the nature of the contamination; 4) availability, cost, and convenience of effective measurement techniques; and 5) masking or other non-target parameters that may cause interferences in measurement. Prior analysis of the contamination from source sampling can be especially useful in identifying key parameters. "Tracers" or "indicators" may be total species indicators, individual species, or ratio of species common to the contaminant source. Ideally, the tracer or indicator will be unique to the contamination source and will not be generally common to the indoor environment.

In the example described by Figure 2, total hydrocarbon (THC) concentration was selected as the Level A parameter. THC can readily be measured using a real-time organic vapor analyzer with a flame ionization detector (OVA-FID) and serves as a good "indicator" that hydrocarbon contaminants are present. The OVA-FID cannot be used, however, to distinguish between the methane and other light hydrocarbons found in natural gas and the heavier hydrocarbons associated with a subsurface petroleum contamination. The natural gas hydrocarbons emitted from a leaky appliance, for instance, could "mask" the instrument's response to the components of interest. Detailed hydrocarbon analyses can confirm the presence or absence of non-methane contaminants in the indoor air. Prior characterization of the subsurface contaminant source through analysis of soil-vapor samples can be used to select the tracer species.

Quality Control Program

Quality control data are required to provide a quantitative assessment of measurement data. Design of structure surveys includes establishing acceptability limits that ensure data quality and collecting quality control data that provide frequent feedback. The two aspects of data quality which are of primary concern are precision and accuracy. Analytical precision is evaluated by analyzing control samples and by performing duplicate analyses of samples. Total sampling/analytical precision, or measurement data variability, is evaluated by analyzing duplicate samples. Variability is expressed in terms of percent difference or coefficient of variation, and these values are compared to

program performance objectives to ensure adequate precision. Accuracy of measurement data is evaluated by analyzing field blank, reagent blank, control, and spike samples. Depending on the type of samples required, accuracy is expressed as analytical baseline concentration, percent recovery, and/or percent difference, and these values are compared to program performance objectives.

Control Data

Monitoring in one or more structures removed from the area of contamination (control structure) provides data describing "typical" levels and species of contaminants in the structure type of interest. Control structure data may also be needed to determine the effects of structure use on levels of key parameters in indoor air. An ideal control structure experiences similar types and schedules of use as the structures being investigated. Depending on the nature of contamination, background levels of key species measured in the control structure may be higher than the analytical baseline levels of the instrument. Control structure data are compared to data collected in other monitored structures to determine whether environmental contamination is influencing indoor air quality.

Documentation and Data Recording

General documentation and data recording requirements include: 1) one or more sample logs for tracking sample collection and shipping; and 2) quality control and calibration logs for tracking instrument performance. In addition, an individual file should be maintained for each structure to be surveyed. The first page in the file serves as a master record of activities and contacts for that structure. Structure address, owner and occupant names and phone numbers, and special instructions are entered on the top half of the page and a record of each visit or contact made in conjunction with survey activities is recorded below. An example Structure Survey and Contact Record from the survey program discussed above is given in Figure 3. Proper use of this form provides documentation of structure entry, helps keep field personnel up-to-date, and ensures responsiveness to owner/occupant requests or comments.

Data collected during surveys is most efficiently recorded on preprinted forms. These forms can be designed based on prior knowledge of the type of structures to be surveyed and can be tailored to meet program objectives. Figure 4 shows a page from the initial survey data form developed for surveys of residential structures. An initial, detailed survey is conducted in each structure to determine the structure layout and overall indoor air quality. Rooms and locations are coded, and point source and breathing zone screening data are recorded. At the onset of this initial visit, the structure layout data form, shown in Figure 5, is completed by the field team. A diagram of the structure is drawn showing walls, rooms, doorways, and other major features. The room designations are then coded with simple combinations of letters and numbers to facilitate computer data entry. Locations where point sources of contaminant infiltration are indicated by screening techniques are plotted on the

layout diagram as an aid to routine monitoring survey design. A copy of the documentation completed during the initial survey accompanies field personnel to all subsequent visits. Use of this material as a reference ensures consistency in data recording throughout the structure survey program.

If routine monitoring is conducted, sampling can be directed to selected rooms in each study structure. An abbreviated version of the initial survey data form is used to record survey data. An example of the routine monitoring form is shown in Figure 6. Location coding developed at the initial survey stage is retained, and sample collection is noted on this form as well as in the sample log. Meteorological and structure activity information is recorded for each survey.

A similar data form is employed for the investigative type structure survey (Figure 7). Under circumstances relating to investigation or emergency response, the initial survey is generally not conducted, and the screening survey data form requires description of each location rather than coding of rooms and point sources. Reasons for the screening survey are documented, and recommendations are made based on the results of screening measurements.

DATA PRESENTATION

Several techniques for evaluating and presenting structure survey data are suggested below. Program objectives, the nature of the contaminant source, and the scope of the survey effort will dictate which of these is most appropriate.

Data Summary and Ranking Checklist

Initially, a data summary is prepared indicating all screening data, sample results, and significant observations for each survey structure. When a large number of structures are surveyed, it is convenient to identify common characteristics in survey results. A ranking checklist is then used to group structures with similar characteristics. One checklist is completed for each structure, and structures with similar types and levels of contaminants are indicated by the grouping of check marks. The ranking checklist used for the example survey program is shown in Figure 8. Similar results indicated four groups of structures based on degree of influence of the contaminant source.

Plots of Contaminant Levels Over Time

Results of routine monitoring surveys can be plotted against time to show trends. Levels or averages of key parameters are plotted for each structure or for a group of structures. Control structure data and/or quality control data are included on the plots to allow quick comparison to background or baseline contaminant levels. Additionally, data may be normalized to show whether a common factor appears to be influencing results in different structures. For example, if concentration data for several structures are divided by their individual average all-time

contaminant value and plotted on a common time scale, a peak occurring on every plot is attributed to a factor influencing all the structures, such as mitigative activities, temperature or weather conditions.

Mapping

Mapping of structure survey results shows whether correlation exists between indoor contaminant levels in structures and proximity of the structures to the environmental contaminant source. Survey results can be mapped as presence or absence (discreet points) or used to define areas of similar indoor impact. To facilitate mapping, locations (grid or coordinates) of survey structures are coded at the initial survey stage.

Statistical Analysis

For large numbers of measurements and samples, statistical analysis is required for data interpretation. Statistics such as maximum and mean value are also required for exposure assessment. Minimum, maximum, mean, median, and standard deviation values are calculated for key parameters in each structure and possibly in groups of related structures.

Statistical treatment of quality control and control structure data is used to establish background levels of key parameters. A general approach to interpretation of low level data involves calculation of the mean and variability of field (or laboratory) blank data and control data to establish baseline and background contaminants, respectively. For example, the mean tracer concentration from control structure data plus three standard deviations on the data may be selected as the background tracer species concentration. Survey data exceeding this value are considered significant and may indicate influence of the contaminant source. Conversely, survey data showing tracer concentrations less than the background values indicate no significant influence.

CONCLUSIONS

Information has been provided to aid in the design of sampling and analytical approaches for monitoring of volatile contaminants in indoor air. The general guidelines given are applicable to possible public health impact associated with subsurface contamination by petroleum hydrocarbons or other volatile organics. The systematic survey approach utilizing different types of surveys, detailed data collection and documentation techniques, and a sampling flow chart to direct the amount and level of sampling and analyses performed was successful in identifying and monitoring indoor air contaminants. The integrated approach provided the data base needed to identify structures impacted by a nearby environmental contamination and to assess public health and safety issues associated with the presence of indoor air contaminants.

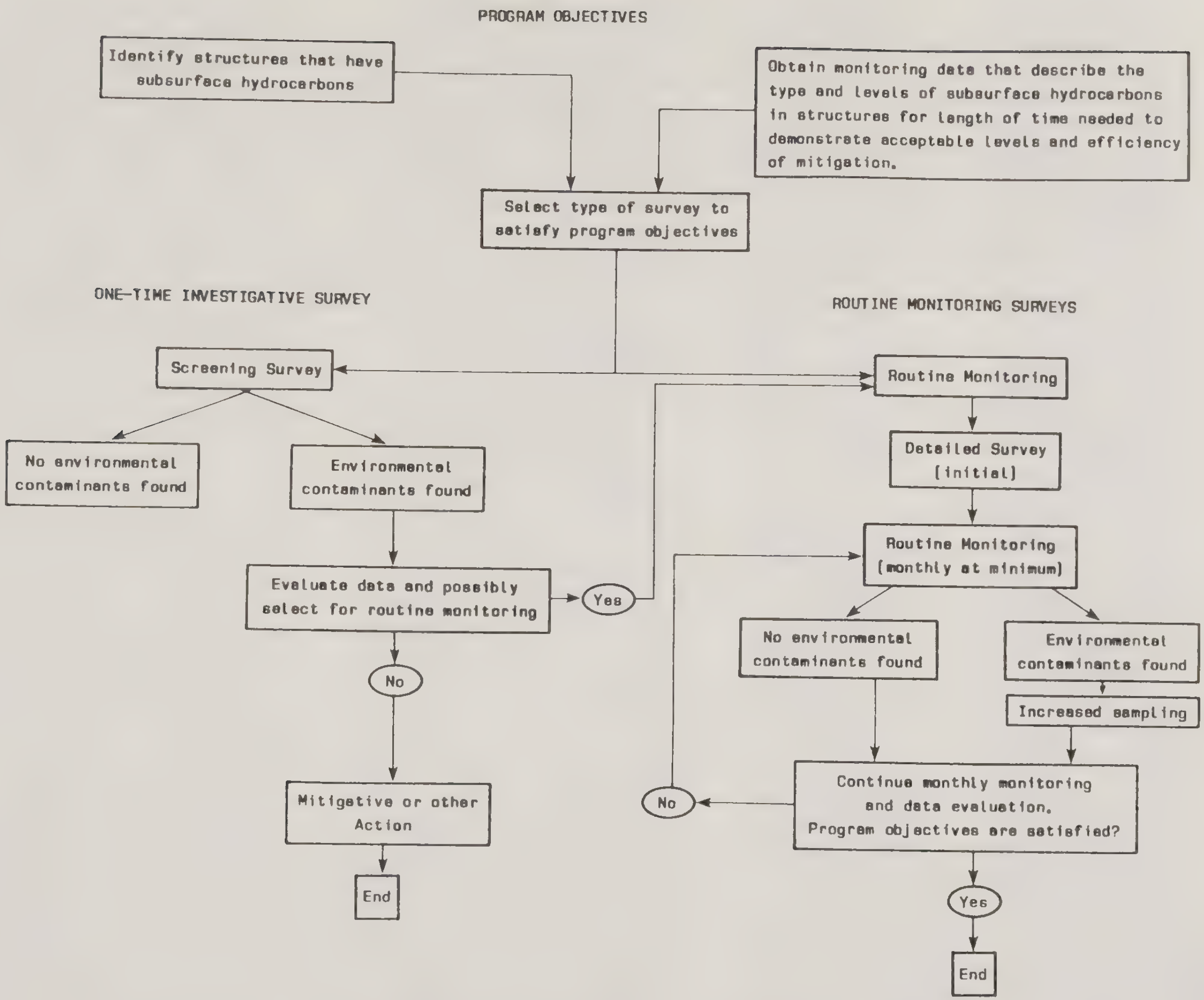
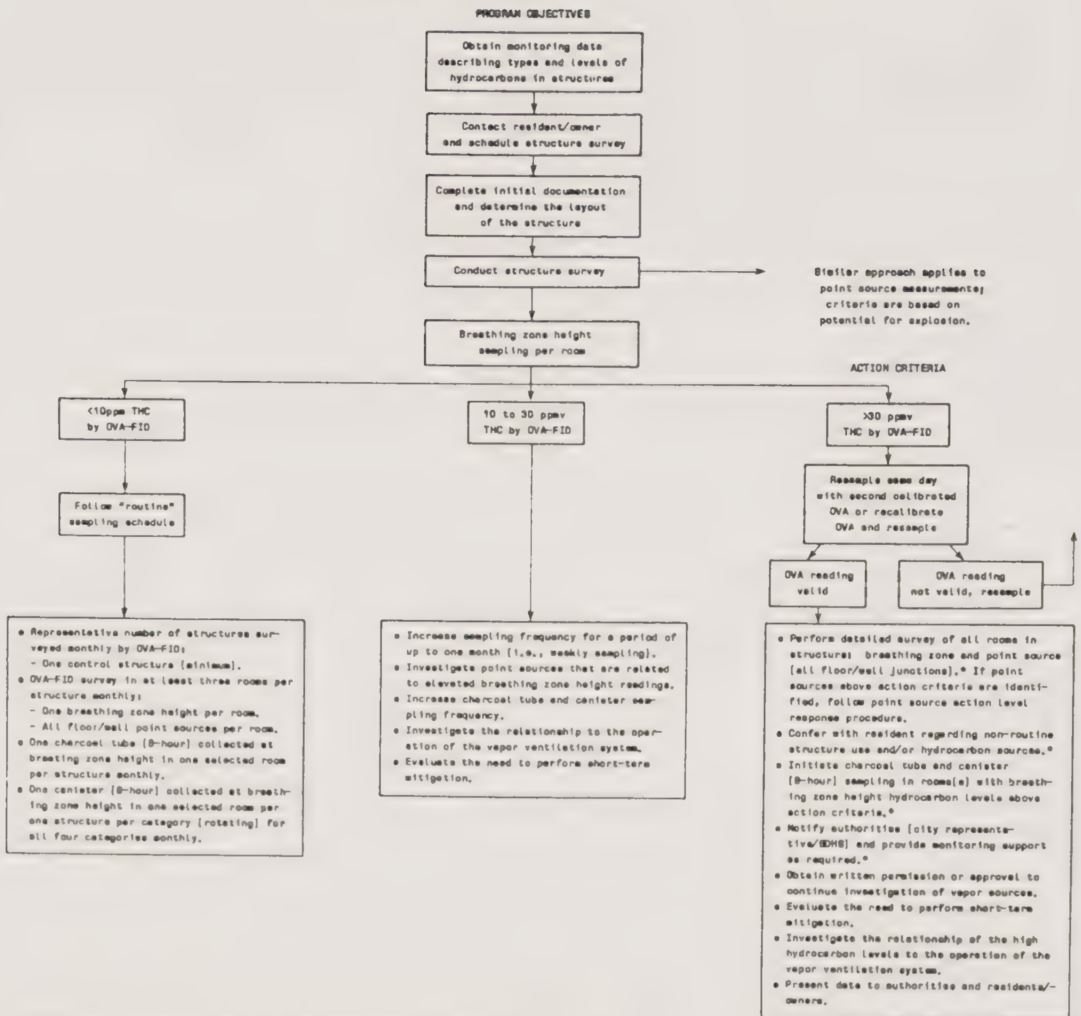


Figure 1. Relationship Between Investigative and Routine Monitoring Surveys



* Activities to be performed on the <u>same day</u> the action criteria is exceeded.

Figure 2. Example of the Flow Chart used for Routine Survey Monitoring of Hydrocarbon Vapors in Residential Structures.

STRUCTURE SURVEY AND CONTACT RECORD

X-COORD ____ Y-COORD ____

X-GRID ____ Y-GRID ____

STRUCTURE ID NO. ________

ADDRESS: ____

OWNER: ____________________ PHONE: (Home) __________ (Work) __________

RESIDENTS: ____________________ PHONE: (Home) __________ (Work) __________

SPECIFIC REQUESTS ON ENTERING /LEAVING STRUCTURE: ____________________

Initials	Date	Screen/Routine Survey	OVA ID No.	Phone Contact With:
1. ________	___/___/___	___S/R___	________	M________________
Comments:				
2. ________	___/___/___	___S/R___	________	M________________
Comments:				
3. ________	___/___/___	___S/R___	________	M________________
Comments:				
4. ________	___/___/___	___S/R___	________	M________________
Comments:				
5. ________	___/___/___	___S/R___	________	M________________
Comments:				
6. ________	___/___/___	___S/R___	________	M________________
Comments:				
7. ________	___/___/___	___S/R___	________	M________________
Comments:				
8. ________	___/___/___	___S/R___	________	M________________
Comments:				

Figure 3. Example of the Structure Survey and Contact Record

INITIAL SURVEY

DATA FORM

X-COORD ____ Y-COORD ____

X-GRID ____ Y-GRID ____

STRUCTURE ID NO. ________

ADDRESS: ______________________________

____

____

DATE: ____________

INITIALS: ____________

OVA-FID NO. ____________

SAMPLING TIME (INTERNAL): _____:_____ AM/PM _____:_____AM/PM

INSTRUMENT BASELINE (ppmv-THC):_____

OUTDOOR AMBIENT (ppmv-THC): _____

ROOM	OVA-FID THC (ppmv)		
ENTRY WAY	IND	PS	PHOTO
EW-1	____	____	____
F/W-N	____	____	____
F/W-W	____	____	____
F/W-S	____	____	____
F/W-E	____	____	____
OTHER PS ________	____	____	____

ROOM	OVA-FID THC (ppmv)		
DINING ROOM	IND	PS	PHOTO
D-1	____	____	____
F/W-N	____	____	____
F/W-W	____	____	____
F/W-S	____	____	____
F/W-E	____	____	____
OTHER PS ________	____	____	____

(remaining rooms appear on following pages)

KITCHEN	IND	PS	PHOTO
K-1	____	____	____
F/W-N	____	____	____
F/W-W	____	____	____
F/W-S	____	____	____
F/W-E	____	____	____
OTHER PS ________	____	____	____

LIVING ROOM	IND	PS	PHOTO
LV-1	____	____	____
F/W-N	____	____	____
F/W-W	____	____	____
F/W-S	____	____	____
F/W-E	____	____	____
OTHER PS ________	____	____	____

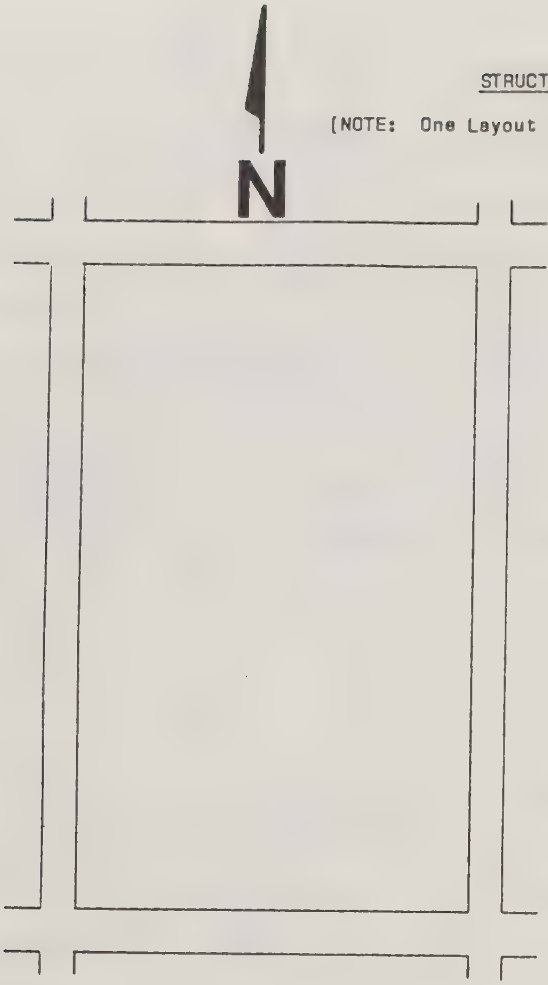
NATURAL GAS APPLIANCES

Type	Room	PS-THC (ppmv)
Stove top	________	________
Oven	________	________
Fittings	________	________
Dryer	________	________
Fittings	________	________
Furnace	________	________
Fittings	________	________
Fireplace	________	________
Fittings	________	________
Other:	________	________
________	________	________

Figure 4. Example of the of the Initial Survey Data Form (first page)

STRUCTURE LAYOUT

(NOTE: One Layout Per Level in Structure)



ROOM KEY

Entry Way	EW- 1
Kitchen	K- 1
Living Room	LV- 1
Dining Room	DN- 1
Bedroom (1-4)	BD- 1-4
Bathroom (1-4)	BA- 1-4
Utility Room	UT- 1
Garage	G- 1
Closet (1-N)	CL- 1-8
Other	O- 1-4
Natural Gas Appliance	NG- 1-9
Point Source	PS
Indoor Air at Breathing Zone Height	IND

INITIALS ________ DATE COMPLETED________ ADDRESS: ________________

____

____

COMMENTS/DESCRIPTIONS: ________________

____

____

____

NOTE: Assign unique number to each room (i.e., BD-1, -2, -3, -4) and indicate walls on layout. Point sources and breathing zone locations where initial measurements made should be drawn in. Record location of highest Point Source (PS) on each wall junction or show as line (-PS-) if same value is found along wall.

Figure 5. Example of the Structure Layout Data Form

ROUTINE SURVEY

DATA FORM

X COORD ____ Y COORD ____

X GRID ____ Y GRID ____

STRUCTURE ID NO. ____

ADDRESS: ____

SAMPLING TIME (INTERNAL): ____:____ AM/PM ____:____ AM/PM

DATE: ____

INITIALS: ____

OVA-FID NO. ____

INSTRUMENT BASELINE (ppmv THC): ____

OUTDOOR AMBIENT (ppmv THC): ____

ROOM	OVA-FID THC (ppmv) IND	PS	CT/CANISTER
BEDROOM			
BD-____	____	____	____
F/W-N	____	____	____
F/W-W	____	____	____
F/W-S	____	____	____
F/W-E	____	____	____
OTHER PS ____	____	____	____

COMMENTS: ____

Meteorological

- Temp (F) — High ____ Low ____ Ave ____
- Wind Speed (mph): High ____ Low ____ Ave ____
- Wind Direction: N ____ S ____ E ____ W ____

LIVING ROOM	IND	PS	CT/CANISTER
LV-____	____	____	____
F/W-N	____	____	____
F/W-W	____	____	____
F/W-S	____	____	____
F/W-E	____	____	____
OTHER PS ____	____	____	____

COMMENTS: ____

STRUCTURE ACTIVITIES:

Ventilated ☐ Yes ☐ No

Comment: ____

Heater On ☐ Yes ☐ No

Air Conditioner On ☐ Yes ☐ No

Recently Occupied ☐ Yes ☐ No

Smoker ☐ Yes ☐ No

Other Activities: ____

KITCHEN	IND	PS	CT/CANISTER
K-____	____	____	____
F/W-N	____	____	____
F/W-W	____	____	____
F/W-S	____	____	____
F/W-E	____	____	____
OTHER PS ____	____	____	____

COMMENTS: ____

VAPOR VENTILATION SYSTEM

Description of Current Operations: ____

Changes in System: ____

INTEGRATED SAMPLING ☐ YES ☐ NO

TYPE: ____ SAMPLE CONTROL NO.: ____ CANISTER ID NO. ____

LOCATION: ____

TYPE: ____ SAMPLE CONTROL NO.: ____ CANISTER ID NO. ____

LOCATION: ____

COMMENT: ____

FOOTNOTES/ABBREVIATIONS

IND — Indoor Air at Breathing Zone Height
PS — Point Source
F/W — Floor/Wall Junction
CT — Charcoal Tube Sample
CANISTER — Canister Sample

N — North
W — West
S — South
E — East

Figure 8. Example of the Routine Monitoring Data Form

INVESTIGATIVE SURVEY

DATA FORM

X-COORD ____ Y-COORD ____

X-GRID ____ Y-GRID ____

STRUCTURE ID NO. ________

ADDRESS: ______________________________ DATE: ______________

______________________________ INITIALS: ______________

RESIDENTS: ______________________________ OVA-FID NO. ______________

______________________________ TIME OF

OWNER: ______________________________ SCREEN: ______________AM/PM

REASON FOR SCREEN: ____

____

SPECIFIC LOCATION	TYPE OF MEASUREMENT	OVA-FID READING ppmv-THC	OTHER SAMPLES COLLECTED
1. ________	IND / PS	________	________
2. ________	IND / PS	________	________
3. ________	IND / PS	________	________
4. ________	IND / PS	________	________
5. ________	IND / PS	________	________
6. ________	IND / PS	________	________
7. ________	IND / PS	________	________
8. ________	IND / PS	________	________
9. ________	IND / PS	________	________
9. ________	IND / PS	________	________
10. ________	IND / PS	________	________
11. ________	IND / PS	________	________
12. ________	IND / PS	________	________

SUMMARY: _______ LIKELY SUBSURFACE HYDROCARBONS _______ NATURAL GAS LEAKS _______ OTHER

RECOMMEND: _______ FOLLOW-UP SAMPLING BY OVA _______ CHARCOAL TUBE _______ CANISTER

COMMENTS: ____

N - NORTH
S - SOUTH
E - EAST
W - WEST

IND - INDOOR AIR AT BREATHING ZONE HEIGHT
PS - POINT SOURCE
F/W - FLOOR/WALL JUNCTION

NAT GAS - NATURAL GAS

Figure 7. Example of the "One-Time" Investigative Survey Data Form

ADDRESS: ____________________

DATE OF EVALUATION: ______________ INITIALS: ________

	OVA-FID	Charcoal Tubes	Canisters
Data Base Entry	○ OVA-FID Survey	○ No samples	○ No samples ○ Canister history indicates high-level contamination
Group 1	☐ breathing zone >30 ppmv THC* ☐ point source(s) >1400 ppmv THC* ☐ repeatedly elevated point source readings in suspect locations (i.e., F/W) that are not typically natural gas sources	☐ THC well above baseline in breathing zone ☐ dominant C_5/C_6 speciation ☐ THC well above baseline in point sources ☐ dominant C_5/C_6 speciation	☐ Tracer species at levels well above baseline levels and in a ratio common to the subsurface plumes in: ☐ breathing zone samples ☐ point source samples
Group 2	☐ breathing zone 10 to 30 ppmv THC* ☐ in several rooms or throughout structure ☐ repeatedly elevated point source readings in suspect locations (i.e., F/W) that are not typically natural gas sources	☐ THC higher than baseline in breathing zone ☐ dominant C_5/C_6 speciation ☐ THC higher than baseline in point sources ☐ dominant C_5/C_6 speciation	☐ Above baseline levels of tracer species: ☐ X ☐ Y ☐ Ratio of tracers near that found in subsurface plumes ☐ Near or below baseline levels to tracer species: ☐ X ☐ Y
Group 3	☐ Breathing zone <30 ppmv, and ☐ elevated natural gas leaks or other point sources identified ☐ single occurrence of an elevated suspect point source ☐ suspect point sources are not elevated ☐ all THC <10 ppmv	☐ THC near or below detection limits ☐ no significant levels of C_5/C_6	☐ Above baseline levels of tracer species: ☐ X ☐ Y ☐ Ratio of tracers near that found in subsurface plumes ☐ Near or below baseline levels of tracer species: ☐ X ☐ Y
Unaffected Structures	☐ repeatedly elevated natural gas leaks or other unrelated sources (i.e., sink drain) identified ☐ suspect point sources are not elevated ☐ all THC <10 ppmv	☐ THC near or below detection limits ☐ no significant levels of C_5/C_6	☐ dominant methane ☐ TNMHC near baseline levels ☐ tracer species common to subsurface plumes not detected, or measured at near baseline levels ☐ unrelated species

Summary Data ○ Group 1 ○ Group 2 ○ Group 3 ○ Unaffected Structures

Comments: ____________________

* Initial survey criteria
THC - Total hydrocarbon
TNMHC - Total non-methane hydrocarbon

Breathing Zone - Measurement in center of room, five feet above floor.
Point Source - Floor/wall seam, utility fitting, crack/conduit in foundation.

Figure 8. Example of the Ranking Checklist.

WORKER EXPOSURES

SCREENING MODELS FOR ESTIMATING TOXIC AIR POLLUTION NEAR A HAZARDOUS WASTE LANDFILL

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Abstract

The emission rate of vinyl chloride from the BKK co-disposal landfill in West Covina, California is estimated. Ambient vinyl chloride concentrations are estimated using a ground level point source model, two virtual point source models, and the simple box model with meteorological and landfill input data representative of periods when ambient monitoring was conducted. The two virtual point source models are most precise and accurate in estimating 24-hour vinyl chloride concentrations. However, the results could include compensating errors in the emission rate and dispersion calculations because the emission rate estimate could not be independently evaluated.

Introduction

Toxic organic chemicals disposed in hazardous waste landfills volatilize over time, diffuse through the soil landfill cover to the surface, are dispersed downwind, and may cause health problems. Three simple screening models have been proposed for estimating toxic air pollutant concentrations downwind of hazardous waste landfills.[1-3] A fourth screening model has been used in similar area source applications.[4]

The use of a landfill emission rate equation with the four screening models is evaluated by comparing calculated and measured vinyl chloride concentrations at two monitoring sites near the BKK Landfill for two 24-hour periods in August 1984. The South Coast Air Quality Management District (SCAQMD) collected the monitoring data. Specific landfill information from BKK is used to estimate the emission rate of vinyl chloride.

Site Description

BKK, located in the Los Angeles basin on the southwestern slopes of the San Jose hills is a co-disposal landfill, having received hazardous chemical waste and municipal waste containing large amounts of organic material since 1963. Disposal of waste solutions from the synthesis of polyvinyl chloride consisting of vinyl chloride monomer and precursors to vinyl chloride, such as ethylene dichloride,[5] were stopped in June 1981 after exceedances of the California ambient air vinyl chloride standard (10 ppb for a 24-hour average) were measured.[6] BKK stopped receiving all hazardous waste in November 1984.

BKK covers 583 acres of which 228 acres contain hazardous and municipal waste.[5] Figure 1 shows the hilly terrain of BKK, which ranges in elevation from 600 to 150 feet msl. Monitoring site A is about 183 meters from the south-southeast landfill border. Site B is about 23 meters from the south border.

Gases from volatilizing organic chemical waste and decomposing municipal waste are extracted by blowers drawing through pipes which extend as deep as 150 feet into the landfill.[7] The collected gases, primarily methane, are burned at the surface in smokeless flares.

Estimating Emission Rates

The emission rate of vinyl chloride from BKK was estimated using Shen's[8] modification of the gas migration equation of Farmer et al.,[9] with an emission rate enhancement factor of 6 which accounts for enhanced gas transport through the soil cover due to anaerobic gas production at co-disposal landfills.[10] The emission rate equation is:

$$E_i = 6 D_i C_{si} A P_t^{4/3} (1/L)(W_i/W) \qquad (1)$$

where:
- E_i = emission rate of chemical i (g/s),
- D_i = diffusion coefficient (cm^2/s),
- A = exposed area (cm^2),
- P_t = Soil porosity (%),
- L = effective depth of soil cover (cm),
- W_i/W = weight fraction of chemical i in the landfill (g/g or ppm),
- C_{si} = pM/RT, the saturated vapor concentration (g/cm3),
- p = vapor pressure (mm Hg),
- M = molecular weight (g/mole),

R = gas constant (6.23×10^4 mm Hg cm^3/mole °K), and

T = absolute temperature (°K).

Eq. 1 assumes that a given concentration of chemical waste will volatilize, resulting in a saturated vapor concentration. The vapor then diffuses through the soil landfill cover at a rate determined by the diffusion coefficient, the cover depth, and the porosity.

The temperature of gases extracted from BKK was 20°C for the March 1984 period[11] and 30°C for the August 1984 period.[5] The measured concentration of vinyl chloride in the collected gases was used to estimate the concentration of vinyl chloride in the landfill.[11] Ten feet was used as the effective depth of the soil cover.[5]

The exposed area used in Eq. 1 varied with different wind patterns. Analysis of wind data and a detailed topographical map of BKK revealed three wind patterns from which landfill emissions could be measured at monitoring sites A and B: nocturnal hillside drainage, nocturnal valley drainage, and daytime sea breeze.

The lack of on-site meteorological data necessitated the use of hourly data from the Ontario International Airport, 15 miles east of the landfill, to estimate landfill wind and stability conditions.[18] Most of the vinyl chloride measured at monitoring sites A and B was a result of nighttime hillside drainage winds.

When the Ontario Airport reported a nocturnal wind direction between 330° and 030°, the wind pattern at BKK was assumed to be hillside drainage. Valley drainage was assumed to occur with nocturnal wind directions at the Ontario Airport of 100° to 110°. All nocturnal wind speeds at the Ontario Airport were 6 knots or less. Daytime wind directions at the Ontario Airport between 270° and 290° were assumed to indicate sea breeze conditions which could result in measured concentrations. The landfill was downwind of the monitoring sites about half of each day during a southwesterly sea breeze pattern.

Table I shows the exposed area, the Table II lists and input values of the other emission rate parameters. Emission rates were calculated for each hour of the five days used in this analysis.

Dispersion Modeling

Vinyl chloride concentrations downwind of BKK were estimated using the following four simple air pollution dispersion screening models:

1. Shen[2] used the Gaussian ground level point source model to estimate ambient PCB concentrations downwind of a landfill containing PCB.

2. Turner[15] approximated a square area source with a virtual upwind point source using the Gaussian point source equation. The virtual point source is located a distance upwind of the upwind area source boundary. This distance, which varies with stability, is chosen to give the virtual point source plume an initial cross wind standard deviation at the upwind area source boundary.

3. The U.S. EPA[1] recommended a similar virtual upwind point source dispersion equation for landfill assessments where the virtual point source is located upwind from the landfill center at a distance equal to 2.51 times the cross wind width of the landfill.

4. Sedefian[3] recommended the simple box model of Gifford and Hanna[16] for landfill assessments.

Hourly ambient vinyl chloride concentrations were estimated with the four screening models and averaged for the 24-hour monitoring periods beginning and ending at 10:00 A.M. local time on March 7-8, 8-9, August 5-6, 6-7, and 7-8, 1984.

Vinyl Chloride Monitoring at BKK

Vinyl chloride monitoring data were collected by the SCAQMD at sites A and B using 24-hour Tedlar bag samples. The samples were analyzed by gas chromatography/flame ionization detection.[7]

Two PVC manufacturing plants are located about 25 miles southwest of BKK, upwind during daytime sea breeze conditions. However, these plants should not affect the concentrations measured at BKK considering the large distance for dispersal and that higher ambient concentrations have been measured near BKK than near these plants. Therefore, background vinyl chloride concentrations around BKK should be near zero.

Results

Table III shows the estimated and measured 24-hour and five-day average vinyl chloride concentrations. All hourly concentration estimates were well below the 8-hour OSHA standard for vinyl chloride of 1 ppm. Some 24-hour estimates and measurements were above the 10 ppb California ambient air quality standard.

The magnitude of the error in the emission rate equation ranged from -113% to 237% of the calculated emission rate.[12] The possible factors behind this error are: variation of the emission rate enhancement factor with the amount of municipal waste; difficulty of approximating the exposed area affecting a monitoring site for this hilly landfill; variation of the depth of the landfill cover from hillsides to flat fill areas.

The use of off-site meteorological data may have led to error in the meteorological input variables. Any error in calculated concentrations cannot be estimated.

The model results were evaluated using the EPA/AMS statistical measures for precision and accuracy[10] listed in Table IV. Due to the lack of measured landfill emission rates, possible errors from the emission rate equation and the screening models cannot be distinguished. The results may include compensating errors from the combination of the emission rate equation and the dispersion models.

The use of models 2 and 3, the two virtual point source models, with the emission rate equation resulted in the most accurate estimations with 97% and 8% average over-prediction, respectively. Overestimating concentrations is a desirable screening model attribute with respect to health and air quality standards, since predictions should be conservative. Models 2 and 3 are also most precise, with the smallest values of noise (the scatter about the mean residual) and gross error (the scatter about zero residual).

Model 3 appears to be more accurate and precise than model 2. However, the data set is too small to conclude this with much confidence. These two virtual point source models do contain appropriate parameters for estimating dispersion from a small area source such as a landfill.

Model 1 was designed for estimating dispersion from a ground level point source rather than an area source. Model 4, the simple box model, was designed for long term averages from an urban area source and would not be expected to per-

form as accurately for a smaller area source such as a landfill. Model 4 also uses neutral stability for 24-hour averages and does not allow for varying stability on an hourly basis to match changing meteorological conditions. Hence, models 1 and 4 are not recommended for landfill assessments.

Conclusions

Two virtual point source dispersion models, used with an emission rate equation, estimated vinyl chloride concentrations near the BKK landfill more accurately and precisely than did the point source or simple box models. The two virtual point source models are recommended for landfill assessments since they were designed for small area sources. THe results could include compensating errors in the emission rate and dispersion calculations, since the emission rate estimate could not be independently evaluated. The emission rate equation should be further evaluated.

Table I. Exposed area of BKK affecting monitoring sites A and B under different wind patterns.

Site	Figure 1 designation	Exposed area (cm^2)	Wind direction	Wind pattern
A	A1	2.60×10^8	330^0-010^0	Hillside drainage
	A2	1.67×10^8	270^0-290^0	Sea breeze
B	B1	0.31×10^8	350^0-030^0	Hillside drainage
	B2	1.86×10^8	100^0-110^0	Valley drainage

Table II. Emission rate input data at BKK for March and August, 1984.

Eq. (1) Variable	March Estimate	August Estimate
D_i (cm^2/s)[a]	0.10726	0.11375
Vapor pressure[b]	2712	3752
C_{si} (g/cm^3)	9.28×10^{-3}	1.24×10^{-2}
A (cm^2)	varies as shown in Table I	
P_t (%/100)[c]	0.20	0.20
L (cm)	304.8	304.8
W_i/W (g/g or ppm)[d]	3.3×10^{-4}	3.3×10^{-4}

[a]Shen[2] [c]Thibodeaux[13]
[b]CRC[12] [d]SCAQMD[11]

Table III. Model estimates and measured vinyl chloride concentrations (ppb) at BKK.

Site	Date	Mar. 7-8	Mar. 8-9	Aug. 5-6	Aug. 6-7	Aug. 7-8	Average
A	Measured	12	5	7	12	9	9
	Model 1	25.1	19.4	40.0	45.7	45.5	35.1
	" 2	9.1	7.3	14.8	16.7	16.9	13.0
	" 3	4.9	4.0	8.0	9.0	9.1	7.0
	" 4	45.9	42.8	76.7	81.1	87.3	66.8
B	Measured	5	7	2	4	2	4
	Model 1	24.3	13.1	30.4	32.4	32.2	26.5
	" 2	11.5	6.1	14.2	15.3	15.2	12.5
	" 3	5.5	3.7	8.4	8.7	8.9	7.0
	" 4	35.5	28.6	62.8	62.0	66.7	51.1

Key

Model 1 = Ground level point source[2]
" 2 = Virtual point source[15]
" 3 = Virtual point source[1]
" 4 = Simple box[16]

Table IV. Performance evaluation summary.

	Concentration average[a] (ppb)	Average residual[b]	Noise[c]	Gross error[d]
Measured	6.5			
Model 1	30.8	-24.3	10.2	27.6
Model 2	12.8	-6.2	4.9	8.5
Model 3	7.0	-0.5	3.6	4.5
Model 4	59.0	-52.4	18.8	58.7

[a]Concentration average is a ten day average, summing both sites.

[b]Average residual = $(N)^{-1}\Sigma\Delta C$; (ΔC = observed concentration - calculated concentration).

[c]Noise = $[(N - 1)^{-1}\Sigma(\Delta C - \overline{\Delta C})^2]^{\frac{1}{2}}$.

[d]Gross error = $[(N - 1)^{-1}\Sigma(\Delta C)^2]^{\frac{1}{2}}$.

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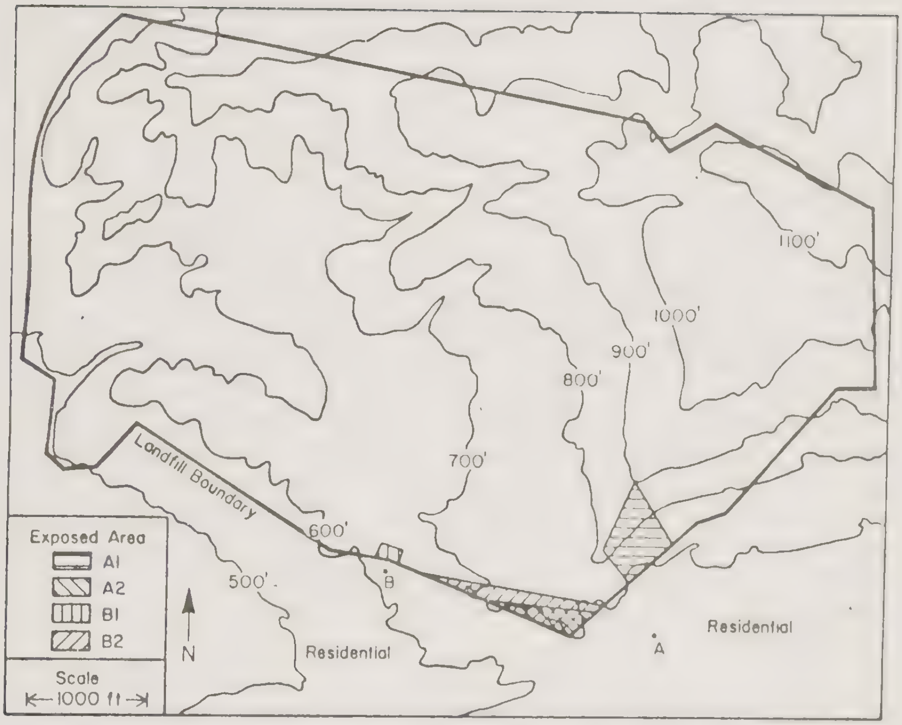

Figure 1. The BKK landfill: topography, location of ambient monitoring sites A and B, and exposed areas used in the emission rate equation.

THE SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT ROLE IN AIRBORNE HAZARDOUS MATERIALS INCIDENT RESPONSE

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INTRODUCTION

Proper management of hazardous materials incidents--uncontained, uncontrolled releases of toxic or hazardous chemicals whether involved in fire, spilled during transportation, illegally dumped, or accidently released from an industrial source--poses a significant challenge to the public agencies responsible for containment, clean-up, and attendant protection of public health and environmental quality. Due to the unpredictable nature of hazardous materials and the wide variety of situations encountered in emergency response, appropriate scene management often includes utilization of the assistance of a varied pool of technical experts familiar with specific aspects of the problem at hand.

The State Hazardous Material Incident Contingency Plan describes pre-emergency preparedness, the state´s emergency management organization, and the scene management system for coordinated response to hazardous materials emergency activities. It further specifies local responsibilities and indicates that local air quality management districts and air pollution control districts are a valuable resource in providing expert advice regarding current and predicted wind patterns and dispersion of airborne pollutants originating from a hazardous material incident. It also notes that some districts can provide sampling, monitoring, and modeling support.

This paper presents an overview of the technical assistance emergency response program developed by the South Coast Air Quality Management District, a regional regulatory agency with jurisdiction encompassing the greater Los Angeles area of Southern California. The response plan utilizes

expanded expertise developed as part of the District's on-going program to control toxic and hazardous air contaminants. This program includes efforts to control and monitor air emissions from industrial sources, active landfills, and remedial waste site contaminant mitigation activities. District hazardous materials specialists from this program respond to technical assistance requests and then coordinate the availability of a wide variety of District resources including meteorologists, chemists, modelers, and engineers. The District currently responds to approximately twenty-five technical assistance requests per year from fire departments, police agencies, and health departments where airborne emissions from hazardous material releases threaten public health.

THE INCIDENT RESPONSE POLICY AND IMPLEMENTATION PLAN

Due to heightened concerns over toxic/hazardous air contaminants and the increasing number of incidents, the SCAQMD Governing Board adopted an initial policy clearly defining the agency's role in hazardous material incident response on September 10, 1982. The policy and subsequent implementation plan were recently reviewed and revised in October of 1985.

The policy recognizes that state law provides that the responsibility for scene management rests with the California Highway Patrol, local police, or the local fire protection agency depending on the circumstances. The District, while not an emergency response agency, serves in a support capacity providing technical assistance, advice, and recommendations within the scope of its authority and expertise in:

a) monitoring air quality,
b) projecting airborne contaminant dispersion patterns, and
c) identifying airborne contaminants.

Following an incident where toxic or hazardous materials have been released to the atmosphere, the policy directs that District inspectors will investigate and review all available information to determine whether any District regulation or applicable section of the California Health and Safety Code has been violated. Violation notices are served where appropriate with subsequent prosecution. In addition, where equipment under a permit to construct or permit to operate issued by the District is involved in an incident, reasonable and necessary action will be taken to require additional permit conditions to prevent or reduce the opportunity for a recurrence of similar incidents.

The District will respond to incidents involving airborne hazardous materials under three circumstances:

1) When requested by the California Highway Patrol, local police or fire protection agency, health department, or other appropriate governmental agency;

2) Where in the judgment of the Director of Enforcement or his designee, support activity will be in the best interest of the public (This procedure may be followed in an attempt to minimize dispatch time should the appropriate governmental agencies take extended assessment time which delays their request for District assistance.); and

3) Where there is good reason to believe that one or more air pollution control regulations are being violated.

The policy limits response activites to personnel who have received special training and who are equipped with appropriate safety equipment. Lastly, the response plan was established subject to annual review and revision to assure effectiveness and consistency with the State Hazardous Material Incident Contingency Plan and various local emergency plans.

Subsequent to policy adoption, an implementation plan was developed to amplify District response policies. The implementation plan contains specific response protocols including:

1) Notification procedure on toll-free telephone line;
2) Internal agency notification and communication procedures;
3) Establishment of "stand-by" duty status to provide 24-hour services and minimize response time;
4) Guidelines for on-site actions; and
5) Definitions of disengagement parameters.

In addition, the second part of the implementation plan defines the personnel and equipment resources dedicated to the response program. This section includes a detailed specification for the minimum content of the training programs required to be completed by response personnel.

THE TECHNICAL SUPPORT CAPABILITY

The current SCAQMD response activities are conducted using a dedicated three-quarter ton emergency response van outfitted with portable contaminant monitoring equipment, a portable anemometer with recorder, safety equipment including protective clothing and breathing apparatus, and a library of reference materials. Portable real-time monitors are carried for organic vapors, hydrochloric acid, chlorine, sulfur dioxide, hydrogen sulfide, and nitrogen dioxide. A large supply of Dreager tubes are maintained to cover a wide variety of additional contaminants. The van is also stocked with evacuated flasks, personal sampling pumps, and other sampling equipment suitable for sample collection intended for subsequent laboratory analysis.

This response vehicle is augmented by two additional air monitoring vans with equipment capable of real-time recorded measurement of specific air contaminants (including oxides of nitrogen, nitrogen dioxide, hydrogen sulfide, and sulfur dioxide); meteorological instrumentation (for surface and upper wind speed and direction, atmospheric stability, and contaminant transport/dispersion through tracer studies); and high volume, impinger, and portable bag samplers.

The District provides support services intended to assist in identifying the nature, concentration, and area affected by a release of toxic or hazardous contaminants to the atmosphere. On-scene activities are coordinated through the Incident Commander. District services available include:

1) Air monitoring
    a) Continuous mobile monitoring for NO_X, NO_2, H_2S, and SO_2.
    b) Monitoring for organic compounds (benzene, toluene, etc.), chlorine, ammonia, acid gases, hydrochloric acid, and other specific contaminants.

2) Providing meteorological information, monitoring, and predictions utilizing field instrumentation and telemetry data from the network of air monitoring stations located throughout the air basin. A field met station is available for protracted incidents.

3) Projecting airborne contaminant dispersion patterns during extended incidents through dispersion modeling.

4) Conducting on-site dispersion monitoring with tracer gas.

5) Assistance in sample collection and analysis to aid in identification of airborne contaminants.

6) Providing facility or industrial process information.

7) Investigation for possible air pollution regulation violations.

An effective response capability requires a high level of coordination and cooperation amongst the agencies and individuals involved. Timely and appropriate on-scene evaluation of an emergency incident requires prior knowledge of potential variables and response methods. Pre-planning and coordinated training are critical. In order to maintain an effective interface with other emergency responders, District response personnel take an active role in multi-agency response training sessions, interagency emergency response planning committees, disaster preparedness scenario drills and exercises with local governmental jusrisdictions, and in post-incident critique sessions.

In addition, to ensure familiarity with District capabilities, many outreach efforts have been undertaken. An outline of the technical support services available and proper assistance request procedures was mailed to all local fire protection agencies along with a complete copy of the District policy and implementation plan shortly after adoption. This information package has also been made available to numerous other agencies involved in hazardous materials issues in conjunction with presentations on program capabilities.

CONCLUSIONS

As with all areas of multi-media environmental concern, efficient and timely resolution of hazardous materials emergencies requires coordinated response and control activities. The South Coast Air Quality Management District´s participation in providing technical assistance and investigative followup to hazardous materials incidents provides a number of benefits to the community-at-large. These include:

1) Availability of air contaminant measurements, meteorological data, and dispersion estimates permit the emergency management agencies to

make better informed decisions regarding safety, exposure, containment, evacuation, and termination of evacuation orders during incidents.

2) Proper handling, storage, and disposal of hazardous materials is encouraged through the deterrent effect created by prosecution of violations.

3) The opportunity is created to review incidents and require controls to prevent incident recurrence.

4) Cooperative working relationships are established in preparation for response to a major incident.

Further enhancement of the real-time monitoring capabilities of the technical assistance team is currently under consideration. Acquisition of a toxic gas monitor with the capability to quantify a number of contaminants commonly encountered in hazardous materials incidents is contingent on available financial resources. In addition, a portable tracer gas monitor is being evaluated for field use during emergency incidents.

Hazardous materials incidents involving the release of airborne toxic or hazardous contaminants pose an inherent threat to the environment and the health and safety of the public and on-site personnel. The District has fielded a knowledgeable and carefully developed technical support team, available to provide assistance to promote the prompt and safe resolution of complex emergency incidents.

OCEAN INCINERATION

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INTRODUCTION AND SUMMARY

This paper presents both a historical and technical overview of ocean incineration - where we've been, where we are now, and where we're headed. It begins with Europe where ocean incineration had its beginnings but where it never really prospered and then traces its evolution in the United States where its progress has been slow and tortuous. This is followed by a technical discussion of ocean incineration requirements, including results of Vulcanus I and II test burns, and concludes with planned future activities in the field of ocean incineration.

THE EUROPEAN EXPERIENCE

Ocean incineration is not new. It dates back 17 years to 1969 in Europe with the advent of the first incineration ship, the Mathias I (1). Since then there have also been the Mathias II, the Mathias III, the Petra (a barge), the Vesta, the Vulcanus I, and the Vulcanus II. Today only the two Vulcanus vessels and the Vesta remain. Several pertinent observations can be made about the vessels and the European experience as follows:

o The vessels were conversions from existing vessels except for the Vesta and the Vulcanus II.

o The vessels were all small (4200 tonnes or less) except for the Mathias III which was 19,000 tonnes.

o They were all designed to burn liquid organic wastes except for the Mathias III which was designed to burn drummed wastes in addition to liquid wastes. However, the Mathias III did not meet emission requirements during its trial burns and was demobilized.

o The Vesta is essentially a captive incineration ship owned by Lehnkering Montan Transport A.G. of West Germany but operated for a group of West German chemical companies headed by Beyer AG.

o Incineration operations are conducted at one site in the North Sea about 50 miles from shore.

o As near as can be determined, the European ocean incineration industry has been borderline financially through the years and has generally incinerated about 100,000 tonnes of waste each year, and some years less.

o Only the Vesta and the Vulcanus II are actively incinerating wastes today. The plan is for the Vulcanus II to be brought to the United States and for the Vulcanus I to replace it in Europe. The Vulcanus I is the original Vulcanus rebuilt in 1983 with a new front hull, new tanks, new piping, and improved incineration controls.

o European incineration ship operations are governed by the regulations that have been established by a United Nations agency - the International Maritime Organization (IMO) which was formerly known as the Inter-governmental Maritime Consultative Organization (IMCO). The authority for the regulations derives from the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (known as the London Dumping Convention) and from the Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk (known as the Bulk Chemical Code). The combustion efficiency requirement is 99.95% $\pm$ 0.05% and the destruction efficiency must be in excess of 99.9% (2). These are less stringent than planned U.S. requirements.

o Although incineration ships have operated in Europe continuously for the last 17 years, there has been a feeling in some quarters that this is a temporary approach. For example, in a resolution on 12 October 1978 in which IMCO adopted certain incineration regulations, it included a clause "RECOGNIZING present methods of incineration at sea as being an interim method of disposal pending the development of environmentally better solutions ...". There was also concern in the Scandinavian countries that acid rain was being generated by incineration ships (2).

THE AMERICAN EXPERIENCE

Initial U.S. Burns

American involvement in ocean incineration dates back 12 years to October 1974 with the initial incineration of 4200 tonnes of Shell Chemical Company chlorinated organic wastes in the Gulf of Mexico by the Vulcanus (3).

Incineration was at a location centered 196 miles Southsoutheast of Galveston, Texas which still remains as the only offshore site approved for commercial incineration in the United States. At that time the Vulcanus was owned and operated by Ocean Combustion Services (OCS), B.V., of Rotterdam, The Netherlands, which was a subsidiary of the Hansa Lines, a German shipping company. It was not called the Vulcanus I until the second Vulcanus vessel was constructed in 1982 by Chemical Waste Management.

The initial incineration continued with three more burns in quick succession of Shell wastes with the last one being completed on January 7, 1975 for a grand total of 16,800 tonnes. The EPA concluded after the initial burn that "the incineration resulted in no significant adverse impact on the environment." (4) In 1977 the Vulcanus returned to the Gulf and incinerated an additional 12,300 tonnes of Shell wastes in a series of burns during March and April. (5,6) Later in the year the Vulcanus was employed by the Air Force to destroy its stocks of herbicide orange which were stored in Gulfport, Mississippi and on Johnston Atoll in the Pacific. The incineration took place off Johnston Atoll 200 miles from shore and consisted of 10,400 tonnes.

U.S. Company Involvement

As a result of the Vulcanus' activity in the United States and the growing hazardous waste problem, Global Marine Development Inc. (GMDI), the Research and Development subsidiary of Global Marine Inc. (GMI), became interested in the possibility of entering the ocean incineration business. Preliminary internal studies were performed, and when the Maritime Administration issued an RFP in May 1977 for a "Study on the Economics and Environmental Viability of a U.S. Flag Toxic Chemical Incineration Ship" (7), GMDI responded and was awarded the contract. This was the first public study on the technical, economic, and environmental feasibilityof incinerating U.S. hazardous wastes at sea.

The study was completed in December 1978 (2). It determined the cost of ocean incineration including transportation of the waste from its source to the seacoast storage area, waste storage, laboratory analysis, ship construction and operation, and incineration. It also projected waste quantities for the United States, Europe, Japan, and South/Central America to the year 1989 and the number of incineration ships that could be economically supported. Study observations are as follows:

o Ocean incineration is less expensive than land incineration because of the economies of scale and because no scrubbers are used.

o Only liquid or pumpable wastes with very low heavy

metal content are suitable based on the then existing incinerator ships. Rotary kilns with afterburners were not investigated since they would have been significantly more expensive and not economically viable at that time.

o The economic viability depends on government regulations governing land disposal of waste such as the Resource Conservation and Recovery Act (RCRA). In other words, strict regulations limiting liquid waste disposal in land fills or wells combined with vigorous enforcement would represent an impetus to ocean incineration.

o The waste streams from three industries are the essential contributers to ocean incineration - organics with 79%, pesticides with 3%, and petroleum with 18% of the total.

o Of the waste quantities estimated to be environmentally and economically suitable for ocean incineration, 88% would be incinerated in the Gulf of Mexico and 12% off the East Coast.

o A total of four ships with a capacity of 12,000 tonnes each would be required for incinerating the available waste.

o Ocean incineration meets the requirements for such operations imposed by the IMCO ocean incineration convention and accepted by the signatory countries. Based on the early Vulcanus I tests in the Gulf of Mexico, including testing of biota in ocean samples in the vicinity of the Vulcanus during incineration, it appeared that there was no adverse effect on the environment.

Based on the promising results from the Maritime Administration study, GMDI proceeded to seriously investigate the ocean incineration business. It updated its ship design, visited the SAACKE company in West Germany which provided the rotary cup burners for the Vulcanus incinerators, issued a procurement specification for incinerators, and designed a tank farm and laboratory. However, the decision was finally reached not to enter the business because there was insufficient commitment from waste generators.

Two companies in the United States have acquired vessels for incinerating toxic wastes. One is At-Sea Incineration which was formed with the participation of a former GMDI employee and was later acquired by Tacoma Boatbuilding Co. Two vessels were constructed with Maritime Administration subsidies, Apollo One in 1984 and Apollo Two in 1985, but never became operational since ocean incineration has not yet been approved by the United States government. The expenditure for the vessels without any

corresponding income has now forced At-Sea Incineration and Tacoma Boatbuilding into bankruptcy.

The second company is Chemical Waste Management (CWM), a subsidiary of Waste Management, which learned from GMDI that the Vulcanus was for sale and then proceeded to buy it in 1980 as an inexpensive way to enter the ocean incineration business. Hansa Lines, the parent company of OCS, became overextended in large oil tankers and went bankrupt. As a result it sold its assets including OCS which owned one vessel - the Vulcanus.

There have been other organizations which have considered entering the ocean incineration business from time to time, but none has made the commitment. Two companies which are prepared to proceed once approval is given are SeaBurn from Greenwich, Connecticutt and Environmental Oceanic Services from Seattle, Washington which plan to use transportable tanks and to scrub the effluent with seawater which would then be discharged back into the ocean (8).

Recent Test Burns

There have been two recent burns in U. S. waters - both with the original Vulcanus, both in the Gulf of Mexico, and both since CWM acquired the vessel. In addition, there was a test burn in Europe for the EPA with the Vulcanus II using special test instrumentation. The Gulf burns occurred in December 1981/January 1982 and in August of 1982. Results are discussed in the Ocean Incineration Requirements and Results section in this paper.

Recent Regulatory and Related Activities

Since there are too many regulatory activities to mention them all, a selection of some of the more pertinent activities are indicated below.

A North Atlantic incineration site has been proposed and a final EIS issued in December 1981 (9); however, the site has not yet been officially approved for commercial incineration operations. It is 179 miles from Ambrose Light at the entrance to New York Harbor.

Proposed Ocean Incineration Regulations were issued on February 28, 1985. Final regulations have not yet been adopted.

The EPA Office of Policy Planning and Evaluation performed an exhaustive study on hazardous waste incineration, both land-based and ocean-based, and issued a 5-volume report in March 1985 (10).

The Science Advisory Board to the EPA also performed a study on incineration of liquid hazardous wastes and issued its report in April 1985. The report concluded that "the operation of both land and sea based hazardous waste incinerators has produced no adverse consequences to the public health or the environment." They also felt that "considerable uncertianty surrounds the data" and recommeded steps to reduce the uncertainty (11).

Prohibition against disposal of non-containerized liquid waste in land fills took effect on May 8, 1985 by direct Congressional action. (12) This prohibition was incorporated into the EPA regulations on July 15, 1985. Proposed additional regulations are tentativel planned for issue by June 1986. These new regulations will specify acceptable absorbents for liquid waste including an absorption pressure test to verify the acceptability of the absorbents. These two sets of regulations combined will provide an increased impetus for incinerating liquid hazardous waste.

Public hearings were held in East Coast cities in January and February 1986 on CWM's request for a permit to incinerate wastes at the North Atlantic site using the Vulcanus II. This would be an instrumented burn with EPA participation. A decision is anticipated by late May or early June of 1986.

Land-based biological incineration tests were completed in March 1986 by the EPA at its Pine Bluff, Arkansas facility. The exhaust gases from PCB incineration were bubbled into sea water continuously for seven days. Different concentrations and dilutions from the seawater were then added to aquarium tanks containing fish and other biota. The objective is to determine the effect on marine life directly as opposed to determining concentrations of hydrocarbons in the exhaust gases and the corresponding destruction efficiencies. Results are not yet available. As far as is known, this is the first time this type of test has been performed.

OCEAN INCINERATION REQUIREMENTS AND RESULTS

International Requirements

IMO's international regulations for incinerator performance are summarized in Table 1. These are in addition to requirements for the incineration ship itself such as double bottoms, double hulls, and compartmentation to minimize the likelihood and severity of waste spills due to collision. Although they aren't as severe as the proposed U.S. regulations, they are considered acceptable by the European countries involved. All test burns in U.S. waters plus the specially instrumented EPA test in Europe of the

Vulcanus II have met the IMO performance requirements.

Table 1

IMO INCINERATOR REQUIREMENTS

Flame temperature	1250° C minimum
Residence time in incinerator	1 second minimum at 1250° C flame temperature
Combustion efficiency	99.95% ± 0.05%
Destruction efficiency	>99.9%
Excess oxygen	3% minimum in stack exhaust
Automatic shutdown	Whenever flame temperature drops below 1250° C
Flame or black smoke above plane of stack	None
Resurvey of incineration system	At least every two years

In addition to incinerator requirements, IMO has also established data recording requirements. These include continuous temperature measurement, waste feed rate, fuel feed rate, carbon monoxide concentration in the exhaust gases, carbon dioxide concentration, vessel location, and vessel course and speed.

Proposed United States Requirements

Although not yet adopted as final rules, EPA's proposed ocean incineration regulations (13) are essentially the same as IMO's except that the destruction efficiency requirements are considerably more stringent. A destruction efficiency of 99.99% (four nines) would be required for all compounds except PCBs, dioxins, and dibenzofurans which would require 99.9999% (six nines). These requirements are the same as for land-based incinerators. The rationale for the more stringent requirements is that EPA believes that they are attainable and that they would provide increased evnvironmental protection.

In regard to IMO's data recording requirements, the proposed EPA regulations require two additional records - the continuous recording of air flow to the incinerators and the concentration of oxygen in the exhaust gases. There is also a requirement for automatic waste feed shutoff whenever

the flame goes out or whenever the wall temperature, oxygen concentration, or carbon monoxide concentration are outside the operating specifications.

In addition to incinerator operating requirements, data recording requirements, and ship construction and operating requirements, there are also port hazardous waste handling requirements imposed by the U.S. Coast Guard.(14) These include handling, storage, loading, and unloading in the port area, and tranfer to and from vessels of ocean incineration wastes.

Initial Vulcanus Burns in the Gulf of Mexico

The first ocean incineration of hazardous wastes in U.S. waters occurred from Oct. 20 to Oct. 28, 1974 and was immediately followed by the second burn from Dec.2 to Dec. 9. (4) The incineration vessel was the Vulcanus. For both burns the waste material consisted of 4200 metric tons of chlorinated hydrocarbons from vinyl chloride process streams and had a specific gravity of 1.3. The elemental composition of the waste for both burns was the same and is shown in Table 2. The composition of the exhaust gases for the second burn is shown in Table 3 (the values were not reported for the first burn). The destruction efficiency for the second burn ranged from 99.987% to more than 99.998% with the average value being more than 99.995%. This meets the EPA's four nines proposed requirement. In more than half of the exhaust gas samples there were no detectable chlorinated hydrocarbons. The 99.995% value is based on the conservative assumption that chlorinated hydrocarbons were present at a level just below the lowest detectable concentration.

Hydrogen chloride (HCl) gas concentrations were measured in the plume from an airplane (second burn). Maximum daily concentrations ranged from 1.8 to 3.0 ppm, were at an altitude of 330 to 790 feet and from 0 to 1300 feet downstream from the incineration ship. Ocean samples were also taken and analyzed for chemical and biological change. Either no changes or barely detectable changes were noted. EPA concluded that there were no adverse effects from plume impingement on the ocean.

Table 2

WASTE COMPOSITION

Constituent	Percent
Chlorine	63%
Carbon	29
Hydrogen	4
Oxygen	4
Heavy Metals	Traces

Table 3

EXHAUST GASES

Component	Percent
Oxygen	10.5%
Hydrogen Chloride	5.5
Carbon Monoxide	43 ppm

The Most Recent PCB Burn

The most recent burn of PCB wastes in U.S. waters took place from 15-31 August 1982 at which time 3507 tonnes were incinerated by the Vulcanus in the Gulf of Mexico. (15) PCB content of the waste was 27.5%, chlorobenzene content was 6.9%, and chlorine content was 37.85% based on analysis of the waste samples that were taken during the actual incineration test runs. These values were slightly different from the truck manifest values. Composition of the exhaust gases is given in Table 4. Combustion efficiency was 99.99%. Although both PCBs and chlorobenzenes were present in large quantities in the waste, they were not detected in the exhaust gases. PCB flow rates to the incinerator varied from 1.28 tonnes per hour to 1.68 tonnes per hour; chlorobenzene flow rates varied from 0.335 to 0.417 tonnes per hour. Average destruction efficiencies of greater than 99.9999% were calculated for both PCBs and chlorobenzenes based on the conservative assumption that they were present in the exhaust gases at a level just below the minimum detectable concentration.

Table 4

EXHAUST GASES, PCB BURN

Component	Percent
Oxygen	10.1%
Carbon Dioxide	9.1
Hydrogen Chloride	2.4
Carbon Monoxide	8 ppm

The Vulcanus II Burn in Europe

In order to confirm the waste incineration capabilities of the Vulcanus II and the destruction efficiencies for volatile, chlorinated, organic compounds, four series of tests were conducted on exhaust gases from 1042 tonnes of vinyl chloride process wastes which were incinerated from February 14-19, 1983 in the North Sea. (16) The elemental composition of the wastes is shown in Table 5, and the exhaust gas composition is shown in Table 6. Combustion efficiency was 99.98%. Destruction efficiencies were determined separately for five different waste constitutents and ranged from 99.998% for carbon tetrachloride to more than 99.999995% for 1,1,2-trichloroethane (seven nines!). These results exceed both the IMO international and proposed EPA national requirements. No 1,1,2-trichloroethane was detected in the exhaust, and the destruction efficiency was conservatively calculated by assuming that it was present in an amount just below the detectable limit. The results for each of the five constituents are shown in Table 7.

Table 5

WASTE COMPOSITION, VULCANUS II

Constitutent	Percent
Chlorine	63.20%
Carbon	25.04
Hydrogen	2.86
Oxygen	8.62

Table 6

EXHAUST GASES, VULCANUS II

Component	Percent
Oxygen	10.8 %
Carbon Dioxide	9.5
Hydrogen Chloride	7.3
Carbon Monoxide	21.4 ppm

Table 7

DESTRUCTION EFFICIENCY, VULCANUS II

Component	Destruction Eff.
1,1-dichloroethane	99.99994%
1,2-dichloroethane	99.99996
1,1,2-trichloroethane	>99.999995
chloroform	99.9996
carbon tetrachloride	99.998

Note that it is the Vulcanus II which is planned for operations in the United States.

Incinerator Ship Controls and Records

It should be noted that the instrumentation and controls on the Vulcanus II and on the Apollo One and Two vessels have been upgraded from those that existed on the Vulcanus during all of its test burns. More parameters are measured and controlled. Measured parameters include carbon dioxide, carbon monoxide, and oxygen concentration in the exhaust gases; fuel, hazardous waste, and air flow rates to the incinerators; wall temperature; flame status (on or off); and vessel course, speed, and location.

There is a computerized data recording system which also automatically calculates combustion efficiency and activates alarms when key performance values (such as carbon monoxide concentration or incinerator wall temperature) exceed set points. There is automatic shutdown. And a permanent record is produced on both floppy disk and computer printout of both incinerator and ship performance.

FUTURE PLANS

Several key events should occur this year which could very well determine the future of ocean incineration in this country. These include:

o A decision by the EPA by approximately the end of May

on whether or not to grant an incineration permit to CMW for an incineration test burn with the Vulcanus II at the North Atlantic site.

o A test burn could occur with the Vulcanus II - the first in both U.S. waters and at the North Atlantic site.

o If a burn occurs, it will be the first use of the biological testing train for ocean incineration and the first test for particulates and heavy metals in the exhaust.

o Issuance of the final rules for ocean incineration.

o The North Atlantic site could be approved for commercial incineration.

o Initiation of a two year EPA research and test program to determine heavy metal emissions in hazardous waste incinerator exhausts.

o Issuance by the Coast Guard of its proposed ocean incineration regulations - more specific and detailed but within the scope of the IMO regualations.

CONCLUSION

The overall conclusion on ocean incineration is that it has been tested on many occasions, has met the international and proposed national destruction efficiency requirements, and no adverse effects have been detected.

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ESTIMATING LANDFILL GAS EMISSION RATES
A METHODS SURVEY

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INTRODUCTION

Municipal solid wastes (MSW) that comprise most landfilled material contain large percentages of paper, wood, cardboard, cotton rags, garden trimmings, and food wastes. These materials are the major contributors to the carbon pool of municipal solid wastes, and the greatest part of the carbon is in the form of cellulose. Tables 1 and 2 show typical solid waste composition and chemical content, respectively. Other organic substances in MSW contribute smaller amounts to the waste carbon pool. These include lipids and proteins in waste food products and a variety of other wastes originating from households and industry.

Table 1. Typical solid waste composition (Tchobanoglous *et al.*, 1977).

Category	Weight Percent
Food wastes	15
Paper	40
Cardboard	4
Plastics	3
Textiles	2
Rubber and leather	1
Garden trimmings	12
Wood	2
Glass	8
Food cans	6
Non-ferrous metals	1
Ferrous metals	2
Soil, ash, etc.	4
Total	100

Table 2. Solid waste chemical analysis (Golueke and McGauhey, 1970).

Substance	Weight Percent
Moisture	20.0
Carbon	29.8
Hydrogen	4.0
Oxygen	25.7
Nitrogen	0.4
Sulfur	0.1
Ash and metal	20.0
Total	100.0

When wastes are first deposited in a landfill, air is present along with variable amounts of water and nutrients, and aerobic decomposition predominates. Under such circumstances, the primary end products of organic waste decomposition are carbon dioxide, water, and heat, plus microorganism cells. After a relatively small amount of organic waste is consumed (the air in the pore spaces can oxidize, at most, a few percent of the available carbon), the waste becomes anaerobic. With the shift to anaerobic conditions, the nature of the decomposition process, and the community of organisms involved, changes markedly. The primary end products of organic waste decomposition become carbon dioxide and methane (the latter under favorable conditions), plus some hydrogen, heat, and microorganism cells.

Under both aerobic and anaerobic conditions, the waste decomposition products include a large gaseous component, which is generically termed landfill gas (LFG). This gas is emitted, under steady-state pressure conditions, at a rate equal to that of net gas generation. LFG generation rates are dependent upon a number of factors and conditions of the waste. These include moisture content, pH, nutrient content, presence of toxicants, temperature, refuse physical properties (e.g., density), and general refuse composition.

There are several reasons why it may be important to estimate LFG emission rates. For example, LFG constitutes a "carrier gas" for trace species that may be present either due to the waste decomposition process or because they were discarded pre-formed. Vinyl chloride, a known human carcinogen, may represent microbial decomposition of certain chlorinated hydrocarbons, and sometimes can be an important trace species in LFG. The gas also frequently contains significant amounts of benzene, toluene, xylenes, trichloroethylene, hydrogen sulfide, amines, and other species with public health and nuisance implications. An accurate evaluation of the nature and extent of landfill contributions to the atmospheric loading of such species can be facilitated by reliable estimates of LFG emission rates.

Another reason for estimating LFG emission rates revolves around the fact that many large landfills emit gas that is about 55% methane, contains about 550 Btu per standard cubic foot, and represents a significant and economically recoverable resource. For some very large landfills, methane generation (and emission) rates can be in the tens of millions of cubic feet per day. For obvious reasons, emission rate estimates are valuable in LFG recovery project planning.

Finally, estimating LFG emission rates can be an important part of the evaluation of LFG migration control systems. Such systems may be intended to reduce sub-surface migration of LFG and/or direct emissions to the atmosphere. It is the latter for which emission estimates are the more useful.

ESTIMATION METHODS: AN OVERVIEW

Methods for estimating LFG emission rates fall into several categories, including:

- o Theoretical computations/modeling
- o Ambient air quality monitoring
- o Soil/waste column characterization
- o Controlled studies
- o Flux measurement
- o Extraction monitoring

The remainder of this paper is devoted to a general discussion of the conceptual and practical bases underlying various LFG emission rate estimation methods falling within the above categories, the associated assumptions, and applicabilities and limitations. It should be noted that certain of the methods to be described are in fairly common use (e.g., extraction monitoring, gas flux measurements, controlled studies), while with others, there is less experience (e.g., heat flux). In the latter case, the discussions to follow are somewhat speculative. Ambient air quality monitoring, which is not a direct landfill-evaluation method, is methodologically well-developed. It has been the subject of numerous papers and reports, and will not be discussed here.

Flux Measurement

Gas generated within landfilled wastes pressurizes the pore spaces, causing advective (forced) flow through the surface cover and into surrounding native soils. In addition, the concentration gradients within the landfill and across the atmospheric interface provide a driving force for diffusive mass transport. The mass transport into the atmosphere, due both to advection and diffusion, can be directly measured. Concurrent with decomposition, heat is generated and is transported through the waste and into the surrounding regions. Heat flux can also be used, at least conceptually, to estimate the LFG generation/emission rate. This is discussed in a later section.

The decomposition process is likely to be relatively steady, on the average, over periods of weeks or months. Accordingly, it may be both practical and appropriate to perform a mass flux survey over a period of several days to weeks. Some part of the gas generated must migrate below surface (except in membrane-lined facilities), suggesting that estimates based on surface manifestations are likely to be biased low. However, a careful evaluation of the landfill in question, along with the local geology, can indicate whether resulting errors are likely to be significant.

Direct measurement of gas emission rates can be accomplished using surface isolation flux chambers, coupled with statistical sampling over the surface of the landfill. The chamber is a vessel that has a large inlet opening on the bottom, which is placed onto or into the surface of the landfill. Provision is also made for passive or active venting of the gas from the chamber, generally near its upper extreme. The change in concentration of methane or carbon dioxide within the chamber can be monitored, and based upon assumed models for mixing of the gas within the

chamber, the landfill gas emission rate can be estimated. Alternatively, the flow rate of the gas itself into the isolation chamber can be measured, although unlike the gas-concentration approach, flow measurement will not account for diffusive transport through the landfill surface.

The use of surface isolation flux chambers for estimating gaseous emission rates from porous media has been attempted by many different investigators including, for example, Getty Synthetic Fuels (unpublished), Dames and Moore (1984), and State of California (1965). Based on past experience, the measurement of gas flux rates appears feasible. It is made difficult, however, by the very small emission rates involved (superficial velocities on the order of an inch per hour) and by environmental conditions (e.g., wind, ambient temperature changes, insolation). In view of the necessary sensitivity of surface isolation flux chambers, careful selection must be made of the season and time for conducting the survey. Night-time hours may be best because of the lack of insolation effects and often improved atmospheric stability. Quiescent atmospheric conditions are generally important in obtaining valid data with surface isolation flux chambers, which may not provide acceptable data if winds are in excess of 3 to 5 miles per hour.

Because the surface isolation flux chamber is used on an extensive porous-medium surface, possibly the single most important design requirement is that the chamber appear transparent to the gas-emission process. In order to achieve this with respect to advective flow, it is necessary that the pressure inside the chamber at the porous medium surface be maintained as near as possible to ambient. This is the case regardless of whether the strategy is to measure flow or to measure the accumulation of some gaseous species, since in either case, deviations from ambient pressure conditions must result in increased or decreased flow into the chamber. Providing a transparent isolation chamber with respect to diffusion is analogous. It requires that the concentration gradient of landfill gas inside the chamber be the same as that in the atmosphere outside the chamber. To the degree the isolation chamber is not transparent to the gas-emission process, biases are likely to result. Under some conditions, the biases may be large and, in general, may be difficult to estimate or correct.

Finally, it should be noted that landfill cover material is commonly fissured, and such fissures may account for a substantial amount of gas released. The extent and importance of these releases can create errors in estimates of emission rates made with a surface isolation flux chamber if provision is not made to account for them.

Soil/Waste Column Characterization

Mass emission rates may be estimated by in-situ measurement of forced (advective) flow and diffusion across the atmosphere-landfill interface. Advective flow may be estimated by sampling the pressure gradient vertically through the soil cover and measuring its gas permeability. One-dimensional flow through the soil cover may be

assumed, and the calculation is straightforward, using an appropriate expression such as that due to Kirkham (1946) or to Green and Duwez (1951), which takes into account both inertial and viscous forces affecting gas flow.

Of the two types of field data required to estimate advective emission rates, gas permeability data are the more difficult to obtain. Pressure measurements may be made by installing probes in the soil column (in-situ) to a depth sufficient to obtain significant pressure gradients. Permeability data may be obtained by collecting soil cores with, for example, a modified California sampler, placing them in appropriately constructed laboratory apparatuses, and plotting flow versus differential pressure ("constant pressure method"). The "falling pressure method" (Evans and Kirkham, 1949) may also be used to directly measure soil gas permeabilities. An indirect method involves measuring the hydraulic conductivity of the soil, and based on relative viscosities, gas permeabilities may be estimated. The resulting data, along with a few readily available constants, allow flow through the landfill cover to be estimated. A statistical statement of the associated uncertainties can be developed provided appropriate sampling methods have been employed.

Several models for diffusive transport are available (e.g., Knudsen and ordinary molecular diffusion), the choice of which depends, in turn, upon the pore structure assumed to exist. For landfills, if diffusion is to be taken into account, it is probably best modeled as ordinary molecular diffusion in view of the large ratio of pore diameters to gas mean free path. The need to estimate diffusive transport, advective transport, or both, depends largely upon forced flow rates. Where forced flow is very large, or if a rough estimate of the emission rate is sought, it may be satisfactory to neglect diffusion. Generally, however, diffusion should be considered, as it may represent a major contributing mechanism for mass transport of LFG from the surface of a landfill. State of California (1965) describes diffusion calculations as applied to landfill emissions.

In general, the above-described method of emission rate estimation is straightforward, requires relatively little in the way of equipment, and is probably less sensitive to climatological variables than is gas flux measurement. Like the use of surface isolation flux chambers for estimating gas emission rates, the present approach does not account for sub-surface gas migration. Although, conceptually, it might be possible to measure LFG emission rates off-site and thereby account for sub-surface migration, this is generally impractical. Accordingly, in addition to a requirement for appropriate temporal and spatial sampling of the site itself, the extent of sub-surface migration and off-site emissions to the atmosphere should be considered, as well as the impact of breaks in the landfill cover.

The measurement of heat flux through the landfill surface is conceptually analogous to measuring gas flux in that temperature represents the driving force, and a heat transfer coefficient allows conversion of the

temperature gradient to the actual quantity of heat released. In general, the energy produced by decomposing waste represents the catabolic energy associated with decomposition of carbonaceous substrates minus that consumed in microbial anabolic processes. Under an assumed chemical model for the overall decomposition of waste to methane and carbon dioxide, the energy released can be converted directly to an LFG generation/emission rate.

Although thermal diffusivities and conductivities of soil may be measured (see, for example, Taylor and Ashcroft, 1972), the overall practicality of a heat-flux approach for landfill application is not well established. The most obvious complication would be effectively filtering out the heat effects due to climatological conditions. A direct, and perhaps satisfactory approach might be to instrument some nearby, off-site area, and to collect data there to use as the baseline condition. Also, because heat flux data are likely to be quite variable, many observations and test locations may be needed for an appropriate statistical treatment.

In an elementary field approach, a system of thermocouples might be buried in arrays oriented vertically through the soil or waste column near the surface of the landfill. The thermocouple array provides the necessary temperature gradient data. The thermal conductivity of the soil may be estimated from published literature, or measurements may be made in the laboratory using relatively simple apparatuses. The net heat flux may then be estimated using the temperature gradient and thermal conductivity data. Alternatively, the use of heat flux plates (Van Wijk and Bruijn, 1964; Van Wijk and Derksen, 1966) may provide better results, this approach eliminating a number of problems associated with variations in thermal conductivity. Once the necessary data have been collected, and based upon an assumed chemical model of landfill gas generation and the associated energy released, it should be feasible to obtain good estimates of gas generation and emission rates.

<u>Extraction Monitoring</u>

Earlier, it was mentioned that the methane in LFG represents an economically recoverable resource. A number of commercial and governmental entities are now engaged in the extraction of methane for this reason. In addition, many landfills have LFG extraction systems in operation in response to regulations and hazards associated with LFG migration. A commonly-used method for estimating rates of LFG generation and emissions is based upon the concept of a "radius-of-influence" (or "volume-of-influence").

The concept, which is commonly used in petroleum engineering and water well hydrogeology, is well established and useful in those fields. With respect to a common application in estimating landfill gas generation and emission rates, however, it can be misleading because it does not account for diffusion away from the surface of the landfill, does not take waste permeabilities into account, and ignores the flow of gas at low velocity but with large flow cross-section. Because of cost issues,

it is impractical to obtain much spatial resolution with this approach, and so it tends also to be inadequate in terms of accommodating spatial heterogeneities within the landfill.

Application of the method begins with installation of one or more gas extraction wells and a system of probes radiating away from them. Landfill gas pressures are measured prior to extracting gas from the wells, and after baseline conditions have been established, various reduced-pressure conditions are imposed on the wells. Under such conditions, the flow rates and landfill gas pressures are measured. Then, either graphically or using curve-fitting methods, a relationship is established defining the distance to which there is "no difference" between the baseline pressure condition and that observed during gas extraction. Ostensibly, such a distance delimits the region of waste within which gas generation exactly offsets gas extracted. Then, given this resulting radius- or volume-of-influence, extrapolation is made to the entire area or volume of the landfill to estimate the overall generation/emission rate.

The concept is flawed in that within media permeable to gas, while there may be some region within which gas generation exactly offsets extraction, this region is difficult to define in practice. It is not necessarily the region within the atmospheric-pressure isobar, nor, certainly, would it be the volume-of-influence as defined earlier. In fact the application of reduced pressures on extraction wells must cause a reduction in pressure everywhere within the gas-generating porous medium. The apparent detection of a distance beyond which there is no pressure effect of gas extraction must necessarily be an artifact of the device used to measure pressure and of natural data variability. Conversely, if the assumption is made that at some distance, pressure changes are negligible, this ignores the large flows that may exist, despite low pressure gradients, due to a large flow cross-section. Furthermore, observed radii-of-influence may be as much a reflection of permeability anomalies as they are an indication of the volume of waste producing the gas extracted.

Because the method, as described here, is based upon faulty concepts, its use is not recommended. In contrast, however, <u>long-term</u> gas extraction and migration control experience with a given landfill probably provides the best estimates possible of rates of emission that would occur were such control system not in place. There is little comfort in this, however, if the objective is to obtain emission estimates quickly or at low cost.

<u>Controlled Studies</u>

Many controlled landfill projects have been documented over the years, and such studies can provide insights into expected LFG emission rates from large landfill sites. Controlled studies can involve real or synthetic wastes, and range in scale from vessels of a few gallons to laboratory lysimeters containing hundreds or thousands of cubic feet of wastes to controlled cells within large landfills. Various issues can be

examined under controlled conditions, such as effects of adding nutrients, of water content, and of temperature, pH, and toxic substances.

Halvadakis et al. (1983) have provided a review of the landfill methanogenesis literature. They include abstracts for a number of studies that present data on LFG generation/emission rates. Table 3, which was reproduced from Halvadakis et al. (1983), gives estimates of such rates under controlled conditions. As the authors point out, emission rates from real landfills may be lower, in view of the less-than-ideal conditions that may prevail in them.

As shown in Table 3, results from laboratory simulators can vary over a considerable range, and there is no reason to discount similar variabilities in real landfills, at least in terms of local generation rate distributions and, perhaps, in terms of total yields as well.

Table 3. Selected total gas production rates from laboratory simulator studies (adapted from Halvadakis et al. [1983]).

	Total gas generation rate, l/kg(dry)/yr	
Source	Average	Maximum
Ramaswami (1970)	57 - 1040	2780
Rovers and Farquhar (1973)	7.25	7.30
Augenstein et al. (1976)	136	438
DeWalle et al. (1978)	.138 - 13.2	54.8
Pohland (1980)	10.2	31.9
Buivid (1980)	25.3 - 488	3160

Notes: A range of results under "Average" indicates more than one set of experimental conditions. "Maximum" is the largest reported or estimated rate obtained during the experiment.

Theoretical Computations/Modeling

Various kinds of computational algorithms can be useful in estimating landfill gas emission rates. Among these are kinetics and transport models. Kinetics models are used to temporally distribute the gas yield ultimately to be generated by the waste. The ultimate yield, in turn, may be estimated from data on waste composition. Transport models, which may account for both advective (forced) flow and diffusion, may also provide estimates of LFG generation/emission.

Emcon (1980) discusses theoretical ultimate gas yields and points out that two different, but related, approaches are frequently taken. In one, which Emcon (1980) terms the "stoichiometric" approach, an empirical formula is derived for the composition of the waste. McCarty (1974), for example, derived an empirical formula for landfilled waste having 99 moles of carbon, 149 moles of hydrogen, and 59 moles of oxygen per mole of nitrogen. The yields of methane and carbon dioxide can be derived from the empirical formula. The other approach, which Emcon (1980) terms the "biodegradable" method, takes into account the likelihood that the various components in MSW may not fully degrade.

Emcon (1980) reports the results of several investigators in computing theoretical ultimate LFG yields, which they point out provides an upper estimate, since real landfill yields are likely to be lower. Based on the stoichiometric approach, yields ranged from 6.6 to 8.0 cubic feet per pound of refuse (wet weight basis). Using the biodegradable approach, results ranged from 3.0 to 5.6 cubic feet per pound of refuse (wet weight basis).

Application of appropriate kinetics model(s) to parcels of landfilled wastes, along with such assumptions as ultimate degree of decomposition, carbon pool losses through leachate migration, and decay rates, allows the calculation of LFG yield over time. Classical Monod kinetics, for example, can be applied to MSW decomposition and LFG yield. Under conditions where substrate is rate-limiting, first-order kinetics may be assumed. Conversely, where substrate is in great excess, the rate of substrate utilization is considered independent of substrate concentration, and a zero-order kinetics assumption is then appropriate.

Another approach is to use zero-order kinetics, but to define the decay rate as a decreasing function of time. This can take into account the idea that different materials and compounds of carbon are likely to decay at different rates. For example, decay rates are likely to be higher for the cellulose in finely divided sawdust or grass than that in chemically-preserved timbers. Over time, the more readily decomposed substrates are consumed, leaving increasingly resistant materials. This might be called a zero-order, declining decay rate model, which is not the same as a first-order model.

A useful consequence of kinetics considerations can be summarized in terms of the following generalization. Regardless of the kinetics actually involved, LFG generation/emission approaches a steady-state rate that is the stoichiometric equivalent of the waste loading rate, taking ultimate biodegradability and carbon losses into account. Furthermore, the rate of approach to steady state depends on the decay rate, and steady state is reached after one decay time. For example, if the loading rate is 1000 tons per month of biodegradable cellulose (with no carbon losses), if one pound of that cellulose is assumed to yield 12 cubic feet of LFG, and if any parcel of the waste decomposes in five years, then the LFG generation and emission rate approach 24 million cubic feet of LFG per month, and reach that steady state rate after five years.

Mass transport models span a considerable range of sophistication. State of California (1965) models carbon dioxide transport across the landfill-atmosphere interface in terms of pure Fickian diffusion, ignoring advective flow. Advective flow can be numerically modeled using a one-dimensional flow expression with a three-dimensional geometric representation, employing finite differences for a dynamic solution, or simultaneously solving mass-conservation expressions to give a steady-state solution. Such an approach can not only provide estimates of three-dimensional advective flow within the waste, but of generation and emission rates and their spatial distributions as well, based primarily upon waste gas pressure and permeability data.

Finally, advective and diffusive models can be combined, to provide a more realistic representation of the mass transport processes resulting in LFG emissions to the atmosphere. ACS (1970) presents a detailed review of state-of-the-art developments in the area of porous media flow. This publication is useful in developing LFG mass transport models.

CONCLUDING COMMENTS

The estimation of landfill gas emission rates is a fundamentally and inherently complex problem. This stems from the large size of many landfills, ill-defined nature of the wastes, differences in landfilling practice, climatological effects, and large number of factors that affect microbial populations. Existing data exhibit tremendous ranges of values. This is the case for estimated decay rates, municipal solid waste compositions, waste particle sizes, landfill moisture contents, gas yields per unit mass of waste, landfill cell sizes, amounts of industrial chemical wastes, and virtually every other landfill characteristic.

The methods presented in this survey paper have good potential, but require much refinement. It is generally the case that landfill gas emission research, and other landfill research areas remain in an immature state, and it appears there are some questionable methods mixed in with the good. It can be expected, however, that the next few decades will see some of the needed refinement in techniques, particularly in view of the recent explosion in interest and concern over hazardous wastes and energy recovery.

It seems most important that near-term landfill research emphasize the development of technically defensible and rigorous methods, and that individual investigators critically review the methods they plan to use. These steps are necessary if reliable methods and data bases are to be developed for describing the behavior of landfills.

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HAZARDOUS WASTE INCINERATION IN CALIFORNIA:
BENEFITS, USES, AND PROBLEMS*

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ABSTRACT

The State of California has led the United States in the development and implementation of more environmentally safe hazardous waste management practices. The single exception to this progressive activity has been incineration of hazardous waste. Repeated efforts by state government to encourage hazardous waste incineration have met with little response from industry. A concurrent result is a slow decrease in the volume of incinerable hazardous waste disposed of off-site, an increasing disincentive to invest in off-site incineration.

This paper reviews the issues surrounding incineration in California, including a review of market demand, incineration activities, competition from other disposal operations, and the regulatory and political forces impacting the growth of incineration as a viable disposal option. Rather than simply blaming the NIMBY (not in my backyard) syndrome for industry woes, the paper provides several constructive observations regarding the impediments to incineration. These include continuing conflicts between state and local politics, the geographic incompatibility of waste source and potential sites (particularly for solids), political and financial risks posed by unclear permitting authority, the high capital cost of a statewide commercial incineration program, and the lack of political muscle to force solid waste, particularly site mitigation residue, to incineration rather than other landfills.

*Presented at HazMacon 1985 (APCA Workshop), Oakland, California, April 24, 1985.

INTRODUCTION
HAZARDOUS WASTE INCINERATION IN CALIFORNIA: BENEFITS, USES, AND PROBLEMS

California industry is rapidly decreasing its dependence on landfill for ultimate disposal of hazardous waste. A major portion of these wastes will soon be treated on-site and/or off-site prior to disposal in so-called residuals repositories. Another significant portion of the state's waste, however, is composed of organic compounds with minor contaminants, waste whose only suitable means of destruction is thermal treatment, or incineration.

The ban on liquids in landfills should force many of these organic wastes to higher cost incineration, resulting in a negligible environmental impact, complete destruction of the waste, and elimination of generator liability. Unfortunately, the relatively low volume of waste combined with its widespread geographic distribution and the political sensitivity of its handling and disposal have combined to effectively block the development of new incineration capacity. Inadequate incineration capacity for these wastes continues to be a problem in California as a result.

In order to better understand why industry is not responding to the apparent lack of capacity with new facilities, it is useful to examine the fundamental factors governing incineration in California today. For the purposes of this paper, these factors will be discussed under the topics of market demand, technology availability, competition, and politics/public opposition. IT Corporation has been the most successful hazardous waste management company in siting new TSD facilities. We believe that an aggressive, technically sound approach to permitting can overcome these impediments.

DEMAND FOR INCINERATION

Numerous studies performed in recent years attempt to consolidate available hazardous waste generation and disposal data for purposes of documenting the need for additional disposal capacity. The principal source of data had been the University of California, Davis study reviewing manifest data from 1979-1980. Subsequent automation of the manifest tracking process has permitted planning authorities to access more accurate data, which has since been used by planning officials in several noteworthy hazardous waste management planning projects. In both cases, the data requires substantial interpretation to account for major site remediation projects, etc. Indeed, the best reported justification for regional incineration facilities has been the volume of incinerable solid hazardous waste generated, not liquid waste.

A review of recent liquid waste off-site disposal figures shows why investment in a regional or statewide liquids incineration facility is not justified. The figures shown in Table 1 represent the generation data provided by the Department of Health Services for 1983. Included in the table are adjustments for large waste categories where only a portion is incinerable under current incinerator design and operating standards. Using established rates for incineration of each category, the approximate maximum annual revenue for a liquids incineration facility is $1,700,000. This estimate does not attempt to account for growing competition from solvent recyclers, the removal of waste to other closer out-of-state locations or the current competition from landfills where stabilization/solidification is an approved method of disposal. Given that the actual revenue would be less than 50% of the above projection, private investment in a new liquid waste incineration facility serving the entire state is not justified.

Solid hazardous waste is more costly to transport and is subject to more competitive disposal rates from landfills. The solid waste figures used by the Air Resources Board in their 1983 study are included in Table 2 and are substantial. Given the high price of incineration for contaminated soils and other materials that can currently be landfilled or landfarmed, a large integrated incineration facility serving the entire State of California cannot expect to receive most of this waste as long as land disposal is permissible. Furthermore, most of the high-volume streams cited in Table 2 (oily waste, pesticides, drilling muds, and miscellaneous organics) are primarily water and would have to be supplemented with even greater volumes of fossil fuel to effect destruction; the cost per ton would be astronomical.

In summary, there is indeed demand for incineration capacity serving California for both solid and liquid hazardous waste. Accurate demand data cannot be developed, however, until riskier competing disposal options are prohibited. Recycling will continue to have a major role in this process as well, though many wastes still cannot be competitively recycled against incineration prices.

STATUS OF CALIFORNIA INCINERATION PROJECTS

According to a Department of Health Services 1984 report, there are ten incinerators operating in California at the present time, only one of which accepts off-site waste. The remaining nine units are situated on-site at various industrial facilities and have long served as part of a manufacturing process in many cases.

The largest commercial facility is the General Portland Cement plant in LeBec, California, which has been granted a permit by DOHS to co-fire waste solvents to supplement the heat input from coal fuel. The plant's rotary kiln is currently limited to burning a maximum of about 20,000 tons per year of liquid organic

waste containing up to 3% chlorine. This constitutes approximately 25% of the total design heat input for the kiln.

The remaining facilities are liquid injection incinerators, mostly operating at generator sites and designed to incinerate fumes and/or liquids from chemical or waste processing. These include facilities at Chevron, Stauffer, and Dow. None of the on-site facilities except Stauffer plan to accept off-site waste or operate commercially. IT Corporation also accepts organic liquid waste for incineration (1000 tons/year), generated from steam stripping, decanting, and distillation at IT's Martinez treatment facility.

Several companies have disclosed plans to build and/or convert existing facilities to incinerate hazardous waste. The most recent proposal came from Genstar Cement Company, proposing to convert their Calaveras Cement Plant in San Andreas to burn liquid fuels, much like General Portland. Chemical Waste Management has informally proposed to construct an incinerator at their Kettlemen Hills land disposal facility. At least one solvent recycler in Southern California has also made it known that they plan to construct a waste solvent incinerator. Several other organizations, including local government agencies, have announced that they are considering burning certain hazardous waste with municipal solid waste in energy recovery incinerators, although the detailed plans have not yet been finalized.

PERMITTING AN INCINERATOR IN CALIFORNIA

Permitting a new off-site hazardous waste management facility is complicated anywhere in the United States, and California is no exception. Permitting an integrated solid/liquid waste incinerator is perhaps the most complex permitting process, as it requires permits for many phases of treatment, storage, and disposal all ostensibly in one facility. Furthermore, while most of the permits are ministerial in nature and reviewed primarily on their technical merits, all of them become discretionary in one way or another.

The key permits for an incineration facility are discussed below. For the time being, permitting of industrial furnaces for hazardous waste incineration is easier than permitting a new integrated TSD facility, due to favorable EPA treatment of industrial waste use as a supplemental fuel, and the probable M3 zoning of most industrial furnaces (which reduces the proponent's exposure to discretionary rezoning opposition). Because the feasibility of constructing a new incinerator for California's liquid waste is questionable, it is more likely that one or more additional industrial furnaces will be permitted for this purpose instead. The permit discussion below addresses the furnace and incinerator regulations separately, where appropriate.

Resource Conservation and Recovery Act (RCRA)

Under the Resource Conservation and Recovery Act and its amendments, hazardous waste incineration facilities are to be permitted as treatment, storage, and disposal facilities and are subject to the standards for each category. Proponents are required to design a facility capable of destroying 99.99% of all hazardous constituents introduced into the incinerator. Testing of this capability is accomplished through a formal trial burn, during which a principal organic hazardous constituent (POHC) is selected, introduced as part of the fuel under normal operating conditions, and its destruction monitored. Performance of the trial burn provides data which can then be used to assess the facility's environmental impact and determine compliance with the destruction requirement. The final permit specifies wastes that can be handled by the facility, using the same POHC and its maximum feed level as "worse case" operating guidelines.

In California, the Department of Health Services (DHS) will be authorized to carry out the intent of RCRA, including incineration permitting, monitoring, and enforcement. In addition to permitting the incinerator itself, DHS will have responsibility for permitting the treatment and storage elements of the facility. Under the current permitting authority in California, the Regional Water Quality Board has authority to permit the facility for protection of ground and surface waters, and the Air Resources Board has the authority to permit the facility for emissions of selected combustion by-products. Because no one has yet attempted to maneuver through this overlapping permitting maze, the complexity and cost of the permitting process is yet unknown. Some elements of the proposed 1985 toxic substances management reorganization may mark a clearer path through many of these rules and thereby provide for a more businesslike permitting approach.

Industrial furnaces, such as cement kilns and industrial boilers, have had a permitting advantage for several years, as they have been exempted from RCRA as supplemental fuel users. As a result, it has been argued that the only major permit required is a process modification permit from the local Air Quality Management District/Air Pollution Control Officer. Permits would also be required for any pre-treatment and storage, but in the case of liquids this is expected to be a minimal effort. Proper fuel selection and safety precautions should in some cases allow for a successful negative declaration under CEQA, i.e. no EIR is needed. Unfortunately, the 1984 RCRA amendments began the process of moving industrial furnaces into the incineration category, regardless of the amount of supplemental fuel used. By 1987, industrial furnaces will be required to obtain permits in much the same fashion as incinerators. Some industrial boilers could be exempt if research indicates they are effective.

In California, few industrial furnaces have been approved for burning hazardous waste as a supplemental fuel. The most

noteworthy example is the General Portland Cement Plant in LeBec, which is permitted by DHS under a long-term research permit to burn supplemental fuels containing up to 3% halogen by weight. Conversations with agencies other than DHS would indicate that state agencies and EPA Region 9 might require that a RCRA incineration permit be obtained for industrial furnaces, even in advance of the 1987 rules. The law will likely include a provision allowing for technical proof of concept rather than actual construction and testing; use of this provision will be left to the discretion of the authorized agency, and considered unlikely in most cases due to public opposition.

Toxic Substances Control Act (TSCA)

The Toxic Substances Control Act governs the disposal of polychlorinated biphenyl (PCB), and exempts PCB management from the requirements of other state and federal regulations. Anyone proposing a PCB incinerator for California would likely be burning hazardous wastes along with PCB, so both RCRA and TSCA permits would be required. The trial burn requirements are different for each, so some consolidation or possible redundancy could also be expected. An industrial furnace attempting to burn only PCBs might arguably be subject to only the local AQMD requirements coupled with the EPA TSCA requirements, circumventing the RCRA requirements except for storage and treatment. Because of PCBs "political volatility," local permitting and EPA permitting should be performed simultaneously.

CASE STUDY: CALAVERAS CEMENT PLANT

To put the above comments in perspective, it is useful to examine a recent case study permitting exercise. In September, 1984, the Genstar Cement Company applied for a permit to test the use of supplemental fuels at their Calaveras Cement Plant in San Andreas. Because of a decline in construction activity in the early 1980's, Genstar closed the cement plant in December, 1982 awaiting a firming of cement prices and possible negotiation of utility and labor concessions at the plant in order to become cost competitive. Genstar saw the use of supplemental fuels as an opportunity to reduce costs. IT Corporation joined Genstar as its technical consultant and fuel supplier on the project.

As in the case of every hazardous waste management facility siting, some valuable lessons were learned in public relations, permitting, and technology. The permitting strategy was to treat the use of supplemental fuel as a process modification at the plant. PCBs were originally proposed as one of the fuel constituents, thereby requiring a TSCA permit as well. Test burn applications were prepared for the county APCO as part of the

process modification, and for Region 9 EPA for PCB. The process application was treated technically as a RCRA trial burn, including carbon tetrachloride as the POHC and proposing to test a relatively high halogen limit in the fuel feed. Permit applications were submitted in September, with testing expected to take place in early 1985.

As a result of the agency and public reaction to both permits, the project has since been down scoped and is continuing along much the same lines as the General Portland project, attempting to burn low halogen supplemental fuels, primarily from Northern California. The original county permit application was never acted upon because of a little known ordinance prohibiting toxic waste disposal in the county (originally intended to ban hazardous waste from sanitary landfills). The EPA PCB application was withdrawn shortly thereafter due to a combination of public pressure and the uncertain future of the project after the county's action. Some of the specific lessons learned are described below.

Permitting Strategy

At the time the permit applications were submitted in 1984, the RCRA industrial furnace regulations still would have allowed a process modification with only two major incineration permits. The trial burn would have been carried out by delivering waste from a remote blending operation at a permitted treatment facility, thereby eliminating the requirement for storage at the site and avoiding unnecessary delay for other treatment and storage permits. While the strategy had merit, there was significant argument from agencies governing treatment and storage about the permitting interpretation. Copies of the permit application were ultimately circulated to those agencies for courtesy review anyway; their exact role on the project and the result of their review were never known due to early withdrawal of the application.

From that permitting exercise, it appeared that the DHS and EPA Region 9 both planned to make a case for RCRA permitting of the facility as an incinerator in advance of the 1987 regulations. Furthermore, EPA and ARB suggested the possibility of a PSD review and air emission limits on compounds such as benzene. These suggestions might now become requirements, although no one will know for sure until a formal permit application is again submitted and processed.

Technology Selection and Justification

The Calaveras Cement Plant, a wet slurry process kiln located in the Sierra foothills, provided an ideal technical setting for hazardous waste destruction. The capabilities of the plant to destroy PCBs were documented earlier by ARB, and were further confirmed by IT engineers as part of the application. However, the dioxin issue looms large in any PCB-related project today,

and of course was brought to the forefront during some preliminary public meetings. While the dioxin formation issue could be dealt with over the long term, the cement plant had been in operation since 1926 and had a history of depositing noticeable quantities of kiln dust in the vicinity of the local high school, some two miles downwind. Despite the well-intended technical arguments about products of incomplete combustion (PIC) and the associated dispersion modeling, the local citizens thought that the exhaust from the plant entered town. This point was brought home by a local state senator during a public meeting on the subject, when he recalled finding kiln dust deposited on his car in the high school parking lot some years ago.

The lesson learned here is that public education about hazardous waste incineration is a long, difficult process. Solid technical homework is needed, as is local political support and technical support from the cognizant agencies. Even then, there will always be an issue that surfaces that was not anticipated. Resolving that issue always means time, and time on a project of this nature always means money.

Definition of Scope and Objectives

As noted earlier, the original scope of the project involved the use of selected supplemental fuels generated in California to augment coal. The proper choice of fuels is always difficult, requiring some detailed market research into fuel supply balanced against public opposition due to people's common knowledge of the fuels properties. Burning PCBs can be an important financial element in an incineration project of this type, but brings with it the greatest amount of public opposition and toughest technical requirements. Selection of a POHC can be done in a way that mollifies the public about its familiarity with the substance, but brings with it the likelihood of the plant burning any compound below it on the list. Local citizens and decision makers will always want to know what is going to be burned at the plant, and their referral to the POHC list will invariably result in selection of the most commonly known and feared toxins on the list. Ideally, an incineration project should choose to simply test specific chemicals that are known to be generated in sufficient quantities in the region in question, in this case California. The amount of market research required to do this properly is substantial.

All along, the primary objective of the project was to make reopening the plant economically viable. Because of the utility and labor issues being debated at the same time, opponents chose to play those issues off against one another. In other words, some accused the proponents of blackmailing the local population into accepting more jobs at the expense of the environment.

Provided that the technical arguments had continued and been resolved, and that labor at the plant was satisfied that all necessary precautions would be taken, success was anticipated but

never had a chance to be achieved. The prospect of reopening the plant and creating jobs at the largest employer in the county did little to dissuade public opposition from those who were fearful of the project's effects.

Politics

Politicians in Sacramento have long recognized the need for more technically sophisticated solutions to the hazardous waste management problems of California. Numerous bills have been proposed promoting incineration, and funding has been provided for several state reports attempting to give the private sector investment incentive. In short, incineration technology is accepted by the political community throughout the state.

The real political problems arise, however, when the chicken comes home to roost, that is, when a project is proposed in a particular politician's own jurisdiction. The local state senator, one of the stronger proponents of "high technology" approaches to hazardous waste management and author of related legislation, was given several private briefings on the project before it became public knowledge, promising to judge the project on its own merits and being assured by the proponents that it would meet his criteria for a safe, effective of disposal. Unfortunately, the Senator chose to use the project as an election issue, terming it a "toxic crematorium" and risking the strong technology-based image he had developed in Sacramento. The Senator's activities went beyond simply criticizing the project, providing substantial fuel to the opposition. Other local politicians who had been briefed on the project as well were less antagonistic, and in several cases quite reasonable. The proponents expected a fair shake in the political arena and did not receive it.

The obvious lesson here is that politics play a significant role in the development of a hazardous waste management project. What made the Calaveras Cement Project unique in this respect is that the proponents best efforts to educate the politicians and hear their concerns before announcing were not taken with the spirit in which they were intended. The end result was a formidable base for public opposition.

Public Education

One of the important siting lessons learned in recent years is that a well educated public can be an ally. While the Calaveras public education plan was well thought out and researched through public opinion polls, etc., project acceptance received a major setback when the local, less experienced public was subjected to substantial outside influence at the urging of several active opponents. In particular, a small coalition of people (the Sierra Coalition Against Toxics, or SCAT) elected to bring in an organized group of professional project opponents from elsewhere in the state to help conduct hearings and develop strategy.

While much of the information put forth to the public from the outside opponents, could arguably be considered inaccurate, the lesson learned was more important: that educating the affected public about the hazards and associated precautions in a facility of this type is not enough in some cases. Many people distrust industry, are more likely to believe what they want to believe from outside sources (whether true or not) and thereby disregard any factual information you present to them. In California, the existence of outside "opponents for hire" is a fact of life, and one which needs to be anticipated when preparing a public education program. In this case, the early exchange of information with key citizen groups backfired by providing selected individuals with the opportunity to plan for strong outside opposition.

CONCLUSIONS

There is a great deal to be learned about siting hazardous waste incineration facilities in California. The best training ground is experience. The lessons put forth in this paper will hopefully be of some value to those considering an effort to permit an incinerator.

It can be concluded from our experience that permitting of a hazardous waste incinerator is possible. The obvious pitfalls were anticipated in our recent experience at Calaveras, but additional lessons were learned and have been passed along to the reader. Each situation is different, but dealing with the technical, environmental, and political issues must take both a thorough and aggressive tone from the start.

It appears that the market for hazardous waste incineration in California is marginal, particularly for liquids and probably for solids. In the absence of some regulatory impetus to remove selected incinerable waste from landfills and require incineration, no firm market data can be prepared. No private entity will take the chance to navigate the permitting maze for the first time and yet still expect to afford the capital investment without some guaranteed return.

Implementation of a major solid/liquid hazardous waste incineration project for California is further complicated by the state's geography and the distribution of heavy industry. Liquid waste incineration demand justifies no more than one major facility, perhaps an industrial furnace. Solids incineration may very well justify a full rotary kiln system or other solids handling facility, but the relatively high cost of incineration and bulk transportation would suggest the need for at least two if not three regional solids incineration facilities. In the absence of better market data and a regulatory incentive to take certain site remediation residues to an incinerator, for example, private industry will not likely make the investment required to serve the entire state.

There are no easy solutions to the problem of the increasing hazardous waste incineration capacity in California. Local political support is critical, trustworthy public education is essential, and the use of state-of-the-art technology will be a prerequisite. Those in a position to develop a major incineration project will certainly await the outcome of the current hazardous waste reorganization in Sacramento, but probably are waiting more for some real action on landfill and surface impoundment regulations. State and federal regulations have indeed created the market for hazardous waste incineration, but without uniform enforcement, it is not possible to project the demand data necessary to justify capital investment.

Table 1. Projected Sources and Types of Prime Incinerable Material Currently Disposed of In California

UCD CODE	DESCRIPTION	CURRENT DISPOSITION (1983 BBLS)
133 (30)	Aqueous Organics (>10+%)	26,940
211	Halogenated Solvents	8,127
212 (15)	Oxygenated Solvents	6.717
213	Hydrocarbon Solvents	3,543
214	Solvent Mix	57,585
221	Waste Oil	23,239
251	Halogenated Still Bottoms	3,633
252	Other Still Bottoms	7,313
350 (10)	Unspecified Liquid Organics	24,811
		161,908

(#) - Estimated % incinerable

Table 2

SUMMARY OF OFFSITE DISPOSAL OF HAZARDOUS ORGANIC WASTE

Type of Waste	Surface Imp. T/Y	Landfill T/Y	Landfarming T/Y	Landspreading T/Y	Steam Stripping T/Y	Incineration T/Y	Drum Burial T/Y	Total T/Y	Total %
Oily Waste #	164,100	63,900	23,000	13,000	0	0	1,300	265,300	43%
Misc. Organic #	13,200	75,500	17,900	10,100	17,400	(2,900)*	17,000	151,100	24%
Drilling Muds #	163,100	13,600	1,100	0	0	0	0	177,800	29%
Pesticides #	18,300	0	0	0	0	0	2,000	20,300	3%
Halogenated	600	1,300	0	1,300	0	(9,100)*	0	3,200	<1%
PCB	0	100	0	0	0	0	400	500	<1%
Total T/Y	359,300	154,400	42,000	24,400	17,400	(12,000)*	20,700	618,200	100%
Total %	58%	25%	7%	4%	3%		3%	100%	

NOTE: The DHS, Report to the Hazardous Waste Management Council on Current Hazardous Waste Generation in California sites 209,000 T/Y for Oily Wastes; 182,000 T/Y for Misc. Organics; 99,000 T/Y for Drilling Muds; 81,000 T/Y for Pesticides; 19,000 T/Y for Halogenated; and 4,000 T/Y for PCBs, totalling 595,000 T/Y.

* This figure is the amount to be incinerated by the General Portland Cement Company. Note that for halogenated wastes the figure is higher than that reported. This is probably due to discrepancies in reporting - e.g. the DHS extrapolated 5 month manifest inventory shows 20,000 T/Y.

** Steam stripping is conducted by the IT Corporation in Martinez, California. IT reports that the 17,400 T/Y contained 1,015 tons of volatile organics which were volatilized in the steam stripping process and then incinerated in a fume incinerator. The 17,400 T/Y is not included in the 442,000 T/Y incinerable waste figure presented elsewhere in this report.

\# Not considered good incineration feedstock (author's note).

Reference: Air Pollution Impacts of Hazardous Waste Incineration: A California Perspective, California Air Resources Board, December, 1983.

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As a registered attendee at HAZMACON 86,
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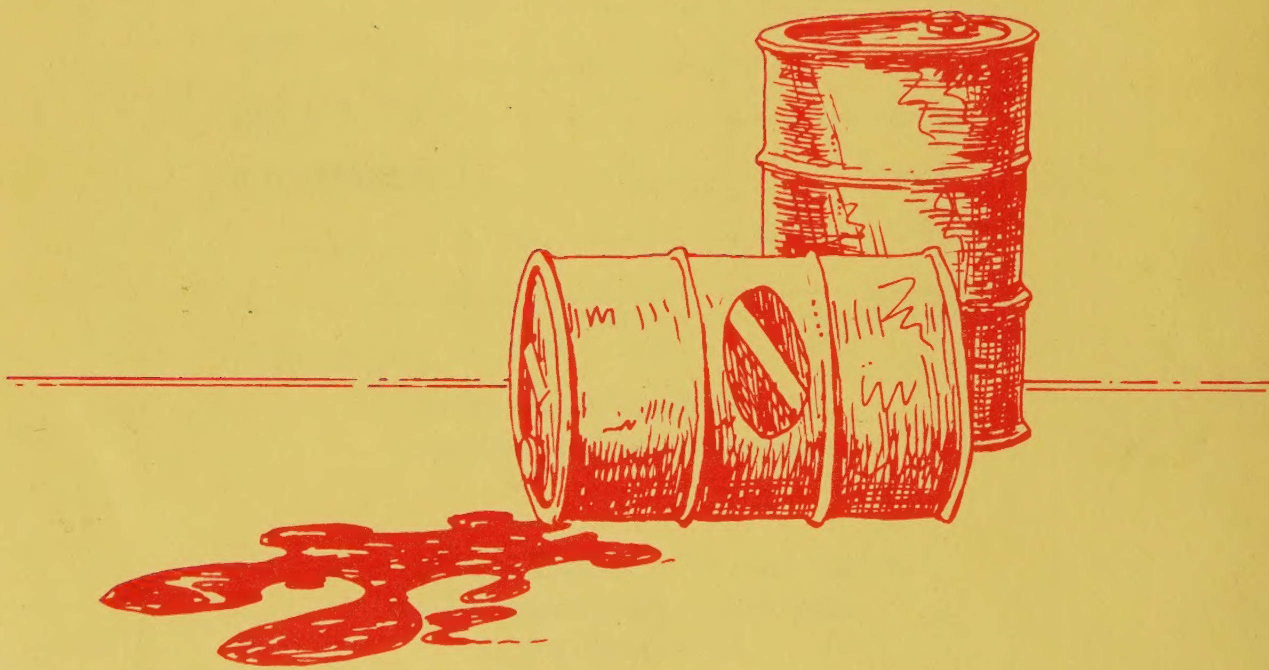
of HAZMACON 87.



ABAG

ASSOCIATION OF BAY AREA GOVERNMENTS

MetroCenter
Eighth & Oak Streets
Oakland
(415) 464-7900

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